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Determination of Lomefloxacin and Gatifloxacin in Urine by High Performance Liquid Chromatography with Polymer Monolith Microextraction

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A method based on poly (methacrylic acid-co-ethylene glycol dimethacrylate) (MAA-EGDMA) monolith microextraction (PMME) was first proposed for sensitive high performance liquid chromatography-ultraviolet (HPLC-UV) analysis of lomefloxacin and gatifloxacin in urine samples. The conditions of PMME were optimized for the improvement of extraction efficiency and reduction of the matrix interferences from urine samples.Under the optimal condition, the eluate solution allowed direct analysis by HPLC. The best separation was achieved within 8 min using a mobile phase of acetonitrile-0.025 mol/L triethylamine (adjust pH to 2.5 by phosphoric acid) buffer solution (33:67, v/v) at room temperature. The proposed PMME-HPLC method exhibited detection limits of 3.4 ng/mL for lomefloxacin (19 ng/mL for gatifloxacin) with satisfactory precision (RSD ≦ 5.7 %) and recoveries between 85.0 % and 106.8 % over a linear range 20-2000 ng/mL (50-1000 ng/mL for gatifloxacin). The proposed method can be used for analysis of lomefloxacin and gatifloxacin in urine samples.

Keywords: High performance liquid chromatography, Lomefloxacin, Gatifloxacin, Polymer monolith microextraction.

INTRODUCTION

The lomefloxacin and gatifloxacin comprise a series of highly potent synthetic antibacterial agents which belong to the fluoroquinolones[1]. Due to their broad antibacterial spectrum and economic advantages, lomefloxacin and gatifloxacin are widely used in human and veterinary medicine worldwide. However, lomefloxacin and gatifloxacin are frequently encountered in clinical and forensic samples which are associated with side reactions and drug overdose. Pharmacokinetics showed that lomefloxacin and gatifloxacin metabolized by urine samples. In order to ensure the drugs are safe for consumption, it is necessary to develop an effective and reliable analytical method of monitoring the lomefloxacin and gatifloxacin in urine samples.

A variety of techniques have been used to determine fluoroquinolones in diverse biological fluids and environmental samples sucessfully, including high performance liquid chromatography (HPLC)[2-8], high performance liquid chromatography-mass (HPLC-MASS)[8-13] and capillary electrophoresis (CE)[14-18] *etc*. However, the sample preconcentration methods are facing great challenge when the analytes of interest are present in a complex matrix such as biological and environmental samples. Among the preconcentration methods, solid phase microextraction (SPE)and liquid-liquid extraction (LLE) are often applied to enrich the analytes and get rid of the sample matrix. Papers had also been published about the determination of fluoroquinolones in biological samples and environmental water samples by HPLC and with C18, Oasis HLB solid phase extraction cartridge[8,19,20]. In order to improve the extraction selectivity, molecularly imprinted polymer (MIP) material was used in high selectivity adsorbent of SPE to eliminate the sample matrix, too[18,21,22]. However, these two methods require multistep procedures which are complex, laborious and time-consuming. Besides, the LLE technique requires large volumes of organic solvents, making it environmentally unfriendly and a potential danger to human health. Therefore, the development of sensitive, simple and rapid preconcentration method is required for multiresidue determination of lomefloxacin and gatifloxacin in a complex matrix.

Recently, polymer monolith microextraction (PMME) based on poly (methacrylic acid-ethylene glycol dimethacrylate) [poly(MAA-EGDMA)] monolith has been found to be a promising sorption material for SPME due to its stability within the entire range of pH, high extraction efficiency to basic analytes and exhibited excellent biocompatibility in dealing

with biological samples[23,24]. This technique has been coupled to reversed phase HPLC (RPLC) in on-line and off-line mode for successful analysis of several analytes from complex matrixs[25-27].

Here, we report a PMME-HPLC method for the simultaneous determination of lomefloxacin and gatifloxacin in urine sample and their chemical structures are shown in Fig. 1. A poly(methacrylic acid-co-ethylene glycol dimethacrylate) (MAA-EGDMA) monolith column was selected as the extraction medium in order to get rid of the interferences from urine sample and improve the LODs of lomefloxacin and gatifloxacin. On the basis of this method, a simple, rapid and sensitive analysis was accomplished to monitor the multiresidue of lomefloxacin and gatifloxacin in the meanwhile.

EXPERIMENTAL

Ethylene glycol dimethacrylate (EGDMA) was purchased from Acros (Sweden). MAA, 2,2'-azobis (2-methylpropionitrile) (AIBN), dodecanol and toluene were obtained from Shanghai General Chemical Reagent Factory (Shanghai, China) and were of analytical reagent grade. The poly(MAA-co-EGDMA) monolithic capillary was synthesized by a polymerization method described previously[28].

Triethylamine [$(C_2H_5)_3N$], phosphoric acid (H_3PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were also purchased from Shanghai General Chemical Reagent Factory and were of analytical reagent grade. Acetonitrile (HPLC grade) was obtained from Fisher Scientific (USA). Purified water was obtained with an Aike apparatus (Aike, Taiwan, China).

Lomefloxacin, gatifloxacin and norfloxacin (used as internal standard, IS) were provided from Xiangfan Center Hospital. A stock standard solution of 1 mg/mL for each analyte was prepared in 25 mM H_3PO_4. The composite standard containing 100 μg/mL of each analyte was prepared by diluting the stock solution with double distilled water. All the solutions were stored in the dark at 4 °C.

Instrumental and analytical conditions: The configuration of the PMME consists of a regular plastic syringe (1 mL), the poly(MAA-EGDMA) monolithic capillary (2 cm × 530 μm i.d.) and a plastic pinhead (one part of the whole syringe). One end of the pinhead coupled seamlessly with the syringe barrel, a metallic needle was removed from the other end of the pinhead and replaced by a 2 cm monolithic capillary (cut from the prepared monolithic capillary) with adhesive. The poly(MAA-co-EGDMA) monolithic capillary for polymer monolith microextraction was prepared by an *in situ* polymerization method as described previously[28]. The pre-polymerization mixture, consisting of the monomer methacrylic acid (MAA) (48 mg), the crosslinker ethylene glycol dimethacrylate (EGDMA) (420 mg), porogenic solvents toluene (110 mg) and dodecanol (860 mg) and the initiator 2,2'-azo*bis*(2-methylpropionitrile) (AIBN) (4.5 mg), was mixed and degassed to remove oxygen. Subsequently, the mixture was allowed to fill a 3-(triethoxysilyl)propyl methacrylate modified fused-silica capillary (2 cm × 530 μm i.d.; Yongnian Fiber Plant, Hebei, China). The capillary was sealed immediately with silicon rubber and then the heat-initiated polymerization was performed at 60 °C for 18 h. The capillary was washed with methanol to remove the unreacted components and porogenic solvents prior to its first use.

The HPLC analysis was performed on an Agilent 1200 HPLC system (Agilent Technologies, Inc., Santa Clara, USA) equipped with an ultraviolet visible (UV-visible) photodiode array detector (G1315D, DAD). The analytical column was a Hypersil ODS column (200 × 4.6 mm i.d.; 5 μm), which was purchased from Agilent Technologies (Palo Alto, CA). The optimized mobile phase for separation was acetonitrile-0.025 mol/L triethylamine (adjust pH to 2.5 by phosphoric acid) buffer solution (33:67, v/v) and the flow rate was kept at 1 mL/min. The detection was performed at 280 nm with the UV detector for analytes.

Norfloxacin stock solution as internal standard was added before HPLC analysis to minimize the variation triplicate injections of the sample were performed and relative peak areas (analyte area/norfloxacin area) were used for quantification.

Polymer monolith microextraction procedure: The whole PMME procedure is composed of four successive steps: preconditioning, sample loading, washing and desorption. A programmable syringe pump (JZB-1800, Jianyuan Medical Technology Co. Ltd., Changsha, China), was employed for the delivery of solutions for PMME. For preconditioning, the syringe was filled with 0.6 mL MeCN, which was then ejected through the monolithic capillary at 0.15 mL/min by the syringe pump and then 0.4 mL phosphate buffer (20 mM, pH 5) was ejected at 0.15 mL/min. After that, the sample solution was ejected at 0.15 mL/min in the same way. In order to eliminate the residual sample solution and the adsorbed sample matrix, 0.2 mL phosphate buffer was kept to flow through the monolithic capillary at 0.15 mL/min. Then the residual solution in the pinhead and monolithic capillary tube was pushed out with an empty and clean syringe to avoid polluting the eluate. For desorption, 0.1 mL CH_3CN-H_2O-CH_3COOH (50:50:0.5, v/v/v) was injected the monolithic capillary at 0.05 mL/min and the eluate was collected into a vial for the subsequent analysis by HPLC. In order to avoid contamination, special syringes were

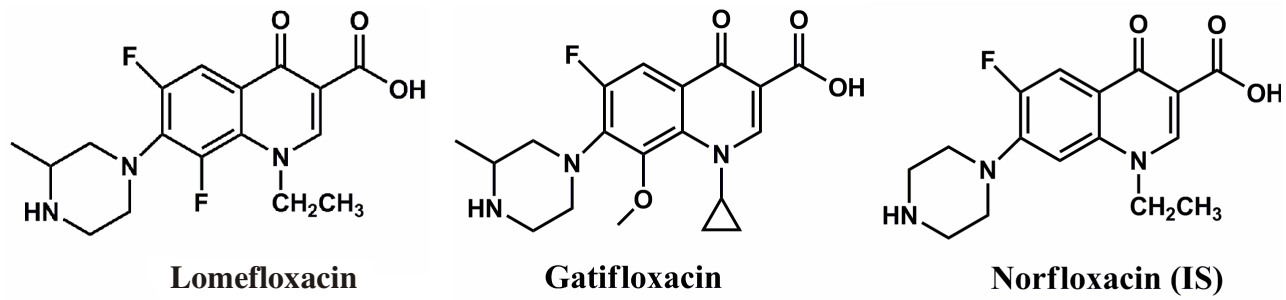

Fig. 1. Chemical structures of the studied lomefloxacin, gatifloxacin and norfloxacin (internal standard)

used for injection sample, buffer and desorption solution, respectively.

Sample preparation: Urine samples were collected from drug-free healthy volunteers. The urine samples were freezing centrifuged at 8000 rpm for 5 min to remove any precipitated materials. Lomefloxacin and gatifloxacin were directly spiked into the supernatant of the urine samples. The urine samples were diluted with an equal volume of 20 mM phosphate buffer (pH 5). The obtained sample at the concentration range 20-2000 ng/mL was used for extraction. Norfloxacin stock solution was diluted in water to the desired concentration and added to the eluate before HPLC analysis to minimize the variation. The urine samples from volunteers receiving lomefloxacin and gatifloxacin were prepared in the same way without spiking. Triplicate injections of the sample were performed and relative peak areas (analyte area/norfloxacin area) were used for quantification. Finally, the sample solution was filtered through a membrane filter (0.2 μm) at 0 °C to remove the suspended substances for the following PMME procedure.

RESULTS AND DISCUSSION

Lomefloxacin, gatifloxacin and norfloxacin can be adsorbed on the silanol group in a reversed phase column, so they are inclined to appear as tailing peaks and affect quantification. Therefore, several buffers and acids added to the mobile phase to avoid their adsorption on reversed phase columns were reported, such as phosphoric acid, disodium hydrogen phosphate, ammonium acetate and triethylamine. The results showed that only a mobile phase containing triethylamine (adjust pH to 2.5 by phosphoric acid) can avoid the effecting of the tailing peaks of the samples.

Optimization of the mobile phase for HPLC separation of the three compounds was accomplished by investigating various volume ratios of 0.025 mol/L triethylamine solution (adjust pH to 2.5 by phosphoric acid) and organic phase. Good separation was achieved with a mobile phase composition of acetonitrile-0.025 mol/L triethylamine (adjust pH to 2.5 by phosphoric acid) buffer solution (33:67, v/v).

Optimization of the poly(MAA-EGDMA) PMME conditions: In order to assess the extraction ability of poly(MAA-EGDMA) monolithic capillary toward lomefloxacin and gatifloxacin as well as to achieve the best extraction efficiency, several parameters, including desorption solvent, extracted sample volumes and the pH of the samples matrix were optimized.

In order to achieve high recovery of the analytes from the monolithic column, the desorption solution was optimized. Different solutions containing CH_3CN-H_2O-CH_3COOH (50:50:0.2, v/v/v), CH_3CN-H_2O-CH_3COOH (50:50:0.3, v/v/v), ACN-H_2O-HAc (50:50:0.4, v/v/v), CH_3CN-H_2O-CH_3COOH (50:50:0.5, v/v/v) were examined. However, only desorption solution containing CH_3CN-H_2O-CH_3COOH (50:50:0.5, v/v/v) enabled no peak of detected in the following blank analysis. It indicated that the ion-exchange interaction had great influence to desorption solution. Therefore, CH_3CN-H_2O-CH_3COOH (50:50:0.5, v/v/v) was chosen as the optimum desorption solution for the subsequent analysis.

The pH of the sample, which influenced the molecule form of the analytes and related closely to the interactions between analytes and the extraction phase, was evaluated in the range of 2-8. As can be seen from Fig. 2, the extraction efficiency is highest around pH 5. The explanation might be based on the fact that lomefloxacin and gatifloxacin were extracted by the monolithic column mostly due to hydrophobic interaction and ion-exchange interaction between analytes and the extraction phase. When the matrix pH value decreased, the samples protonated completely and the amount of the ionized carboxylic groups decreased. These resulted in the ion-exchange interaction between the polymer and samples weakened and the extraction performance became poor. When the matrix pH increased, the amount of the ionized carboxylic groups decreased either. These resulted that the ion-exchange interaction between the polymer and samples weakened and the extraction efficiency decreased. It is obvious that the highest extraction efficiency resulted from the equilibrium of the two interactions and thus pH 5 was selected for the subsequent analysis.

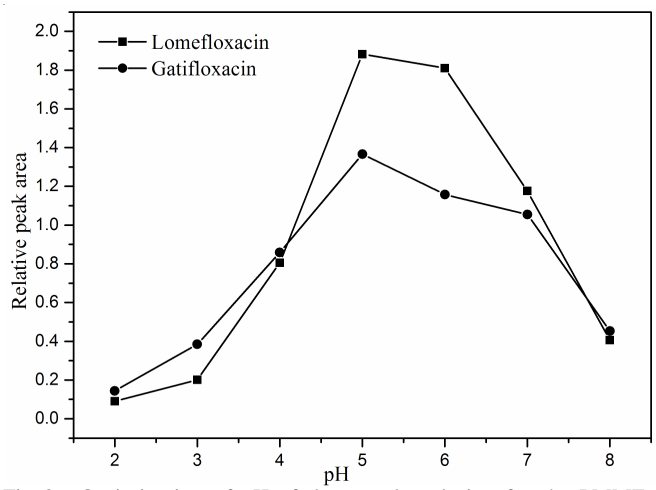

Fig. 2. Optimization of pH of the sample solution for the PMME. Lomefloxacin and gatifloxacin were spiked in 20 mM phosphate buffer at different pH at 0.2 μg/mL. Norfloxacin (IS) was added after PMME with the concentration of 1 μg/mL

The extraction equilibrium profiles were monitored by increasing the volume of the extracted sample from 0.5 mL to 4 mL at a constant extraction flow rate. As shown in Fig. 3, the peak areas increased with increasing the volume of the extracted sample up to 4 mL. In order to shorten extraction time, a sample volume of 1 mL was selected for subsequent analysis with satisfactory sensitivity achieved.

The chromatogram of lomefloxacin and gatifloxacin obtained by PMME-HPLC and direct HPLC analysis under the optimized conditions are shown in Fig. 4. Comparing the chromatogram obtained by PMME-HPLC (Fig. 4a) to that of the direct injection (Fig. 4b), a dramatic peak height enhancement was found, indicating the remarkable preconcentration ability of the monolithic column.

Analysis of lomefloxacin and gatifloxacin in human urine: In order to eliminate matrix interference of biological samples, a wash step should be applied immediately after the extraction. After extraction, 0.2 mL solution of 20 mM phosphate buffer (pH 5) was kept to flow through the capillary as the wash step. It was demonstrated that the extraction efficiency of the analytes was uninfluenced by the wash step.

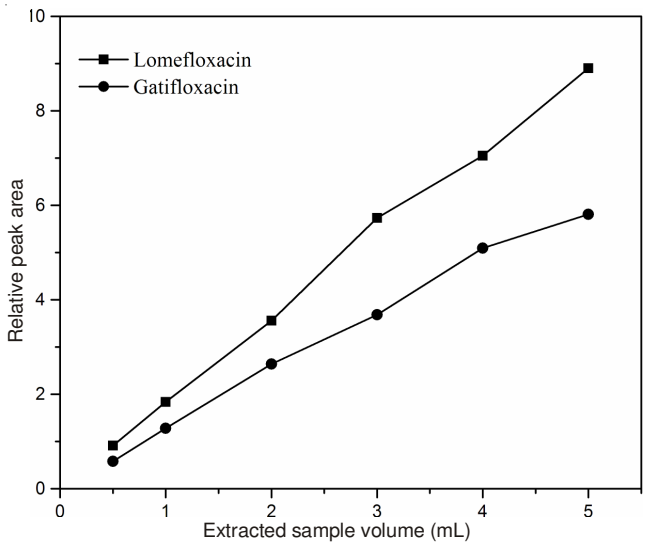

Fig. 3. Extracted sample volume profile of the lomefloxacin and gatifloxacin for the PMME. Lomefloxacin and gatifloxacin were spiked in 20 mM phosphate buffer (pH 5) at 0.2 µg/mL. Norfloxacin (IS) was added after PMME with the concentration of 1 µg/mL

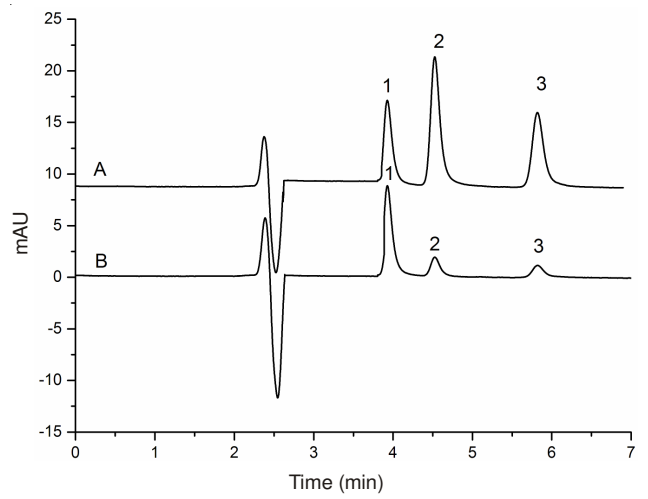

Fig. 4. Chromatogram of lomefloxacin and gatifloxacin standard sample obtained by PMME-HPLC (a) and direct HPLC analysis (b). Peaks: (1) norfloxacin (IS) (2) lomefloxacin (3) gatifloxacin. Lomefloxacin and gatifloxacin were spiked in 20 mM phosphate buffer (pH 5) at 0.2 µg/mL. Norfloxacin (IS) was added after PMME with the concentration of 1 µg/mL

Fig. 5a and b show the representative chromatogram comparing PMME of human urine spiked analytes with blank urine after the same treatment, which indicates that almost no matrix interferential peaks influencing the quantification of the analytes were observed. The result indicates that the PMME technique was ideal for urine sample analysis, which integrated the preconcentration and removal of sample matrix as a whole.

In order to validate the linearity of the PMME-HPLC method, calibration curves were constructed with the lomefloxacin spiked to the urine samples in the range of 20-2000 and 50-2000 ng/mL for gatifloxacin. In all the cases, a constant amount of 1 µg/mL norfloxacin was added as IS. Linear regression analyses were performed using ratios of peak areas of lomefloxacin and gatifloxacin to that of IS against the respective concentration. The results are listed in Table-1. The regression

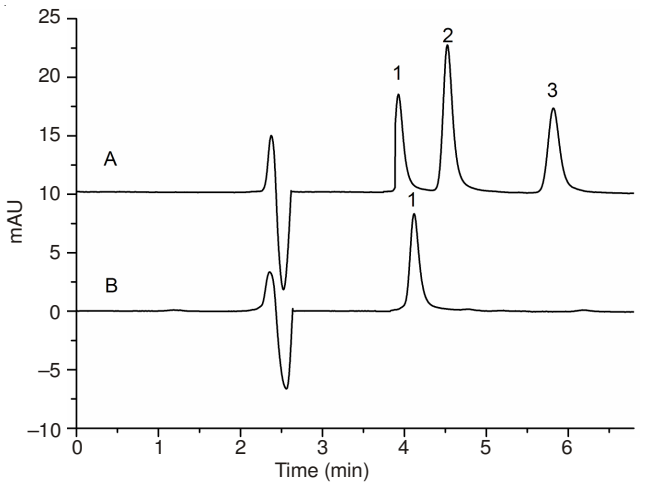

Fig. 5. Chromatogram obtained by PMME-HPLC of spiked urine (a) at 0.2 µg/mL; PMME-HPLC of blank urine (b); Peaks: (1) norfloxacin (IS) (2) lomefloxacin (3) gatifloxacin. Norfloxacin (IS) was added after PMME with the concentration of 1 µg/mL

coefficients (r) were better than 0.9980 and the detection and quantification limits were also calculated with the S/N set at 3 and 10, respectively, which were found to be more than adequate for the usual analytical requirements for controlled drugs analysis in pharmaceutical experiment. Especially, the detection limition of lomefloxacin was lower than that of applying SPME/LC/MS/MS (5.8 ng/mL)[13].

TABLE-1
CALIBRATION PARAMETERS FOR PMME-HPLC OF LOMEFLOXACIN AND GATIFLOXACIN FROM URINE

Comps.	Linear range (ng/mL)	Calibration curves			LOD (ng/mL	LOQ (ng/mL)
		Slope	Intercept	r		
Lomefloxacin	20-2000	8.89615E-4	0.08144	0.9981	3.4	11.3
Gatifloxacin	50-2000	0.00108	-0.03177	0.9980	19	57.1

Number of data point for calibration curves is 5 and three repetition per point. Extraction conditions and HPLC conditions were outlined in section experimental and discussion.

The extraction recovery of the method was also calculated by comparing the extraction efficiency obtained by extracting spiked urine samples to that of the standard sample, with the results listed in Table-2. Good recoveries were obtained for all the analytes in urine A (between 85.0 % and 106.8 % with the relative standard deviation (RSD) values between 1.4 and 5.1 %). These results confirmed that the urine matrix (*e.g.*, inorganic salt and protein) hardly affected the extraction under the optimized conditions. For further validating the method, analytes spiked in urine (B-E) obtained from different volunteers were analyzed and RSD for five measurements were below 8 %, which confirmed that the method for extraction of lomefloxacin and gatifloxacin from urine samples was robust and reliable.

The reproducibility of the developed method was determined by the inter-day and intra-day precision. Three levels of sample concentrations were tested. As shown in Table-3, the intra-day and inter-day precisions of the relative peak areas, which were calculated as relative standard deviation for five measurements, were lower than 6.3 % for lomefloxacin and 8.6 % for gatifloxacin, respectively.

TABLE -2
RECOVERY AND PRECISIONS AT THREE DIFFERENT CONCENTRATIONS
FOR PMME-HPLC OF LOMEFLOXACIN AND GATIFLOXACIN FROM URINE SAMPLES (A-E)

Compounds	Concentration (ng/mL)	Recovery (%, RSD, %)				
		A	B	C	D	E
Lomefloxacin	100	90.5 (1.4)	99.3 (3.3)	103.6 (3.5)	92.2 (1.4)	84.7 (3.4)
	500	92.3 (4.5)	92.5 (8.0).	98.4 (3.3)	95.4 (5.3)	92.8 (4.5)
	1000	99.8 (2.5)	101.2 (4.6)	104.3 (2.1)	104.3 (1.7))	100.4 (3.5)
Gatifloxacin	100	90.7 (5.1)	103.3 (4.4)	93.6 (2.3)	93.1 (2.4)	87.3 (5.3)
	500	88.6 (2.0)	90.8 (4.1)	85.5 (3.3)	85.0 (3.7)	89.6 (2.0)
	1000	106.8 (3.1)	98.5 (6.4)	98.9 (2.8)	95.3 (1.2)	103.0 (5.1)

TABLE-3
INTRA-DAY AND INTER-DAY PRECISION OF RELATIVE
PEAK AREAS AT THREE DIFFERENT CONCENTRATIONS
FOR PMME-HPLC OF LOMEFLOXACIN AND
GATIFLOXACIN FROM URINE SAMPLES

Compounds	Concentration (ng/mL)	Precision (R. S. D., %)	
		Intra-day (n=5)	Inter-day (n=3)
Lomefloxacin	100	3.7	3.4
		6.0	3.8
	500	3.4	3.2
		2.4	6.3
	1000	5.7	5.5
		4.0	3.7
Gatifloxacin	100	5.5	4.6
		8.6	7.1
	500	3.0	3.4
		2.0	5.3
	1000	4.3	5.3
		2.0	4.2

The intra-day precision were calculated by performing 5 extraction of independently prepared urine samples with analytes spiked at three different concentrations over a day. Inter-day precisions were accessed by performing 3 extraction of independently prepared urine samples with analytes spiked at three different concentrations for continuous three days

Conclusion

The triethylamine solution (adjust pH to 2.5 by phosphoric acid) was applied to resolve the tailing peaks of lomefloxacin and gatifloxacin successfully and then poly(methacrylic acid-co-ethylene glycol dimethacrylate) monolith microextraction followed by HPLC was able to extract and detect the lomefloxacin and gatifloxacin in urine samples. In view of the simplicity, low cost, rapidness and sensitivity, the present method is recommendable.

The method exhibits good precision, reproducibility and linear response over a wide concentration range. Moreover, since the extract by PMME can be directly analyzed by HPLC, the PMME method is rapid and easy to use compared with the other extraction method coupled with HPLC.

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