

Rapid Limit Test of Eight Quinolone Residues in Food Based on New Limit Test Method: TLC-SERS

Supplementary Materials

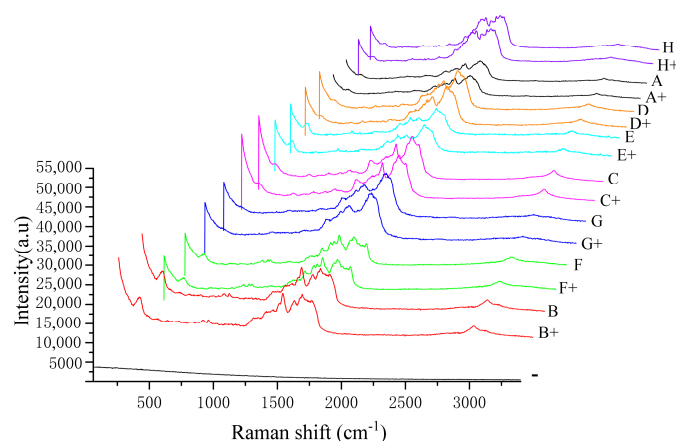


Figure S1. The SERS of the eight quinolones in the simulated positive sample by the TLC-SERS. (H, A, D, E, C, G, F, and B represent Nadifloxacin, Enrofloxacin, Fleroxacin, Sparfloxacin, Ofloxacin, Gatifloxacin, Enoxacin, and Ciprofloxacin, respectively. H⁺, A⁺, E⁺, D⁺, C⁺, G⁺, F⁺, B⁺ represents Simulated positive samples containing H, A, D, E, C, G, F, and B; “-” represents Negative sample.)

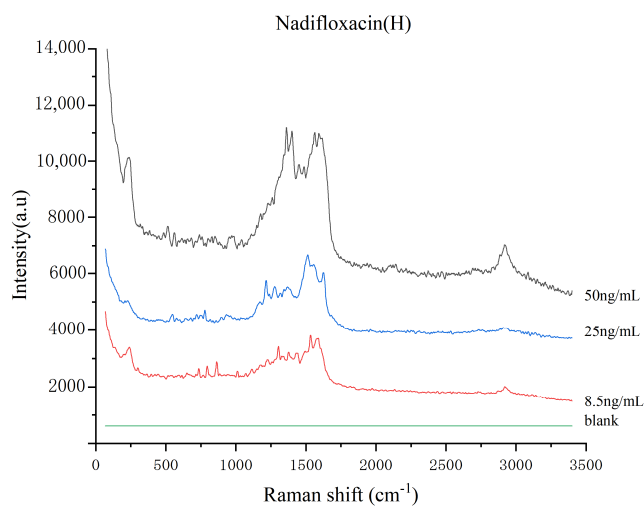


Figure S2. The SERS of the nadifloxacin (H) of different concentrations by the TLC-SERS.

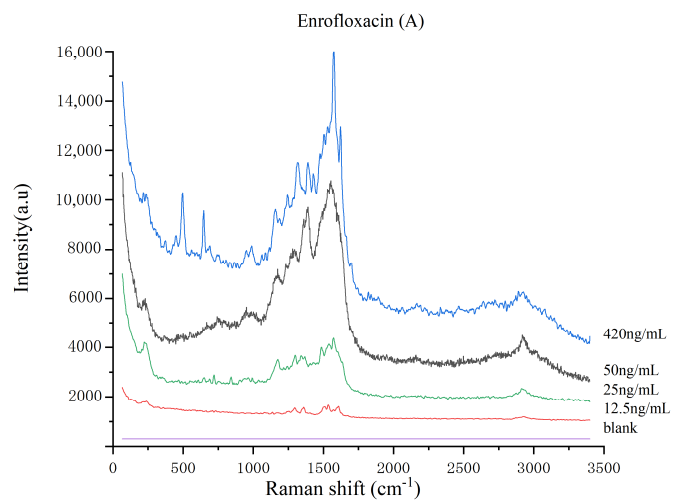


Figure S3. The SERS of the enrofloxacin (A) of different concentrations by the TLC-SERS.

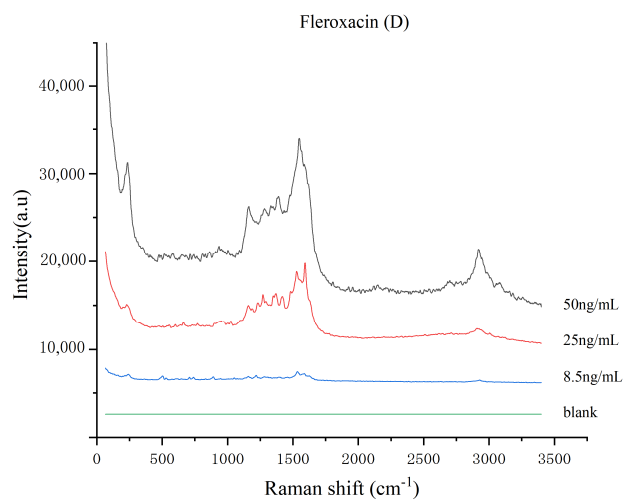


Figure S4. The SERS of the fleroxacin (D) of different concentrations by the TLC-SERS.

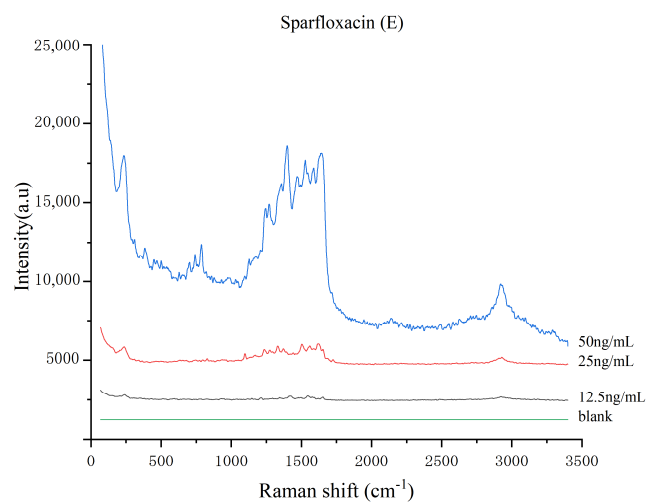


Figure S5. The SERS of the sparfloxacin (E) of different concentrations by the TLC-SERS.

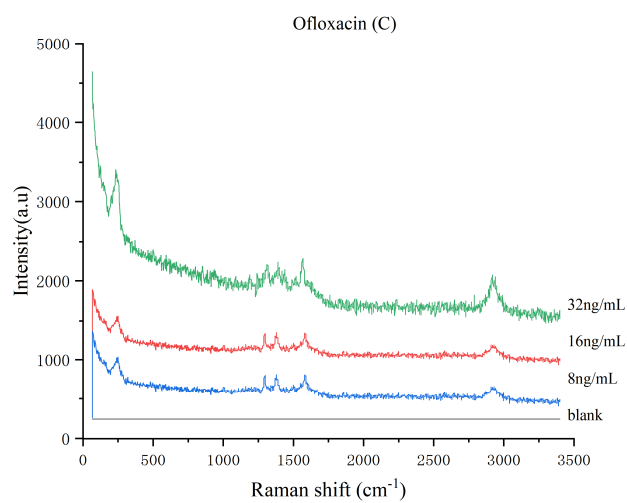


Figure S6. The SERS of the ofloxacin (C) of different concentrations by the TLC-SERS.

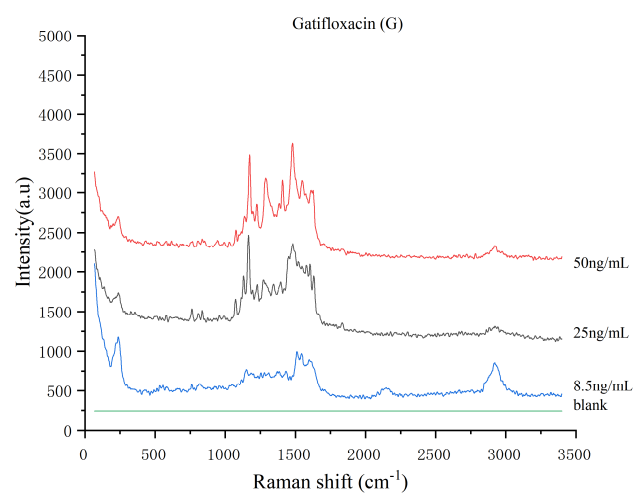


Figure S7. The SERS of the gatifloxacin (G) of different concentrations by the TLC-SERS.

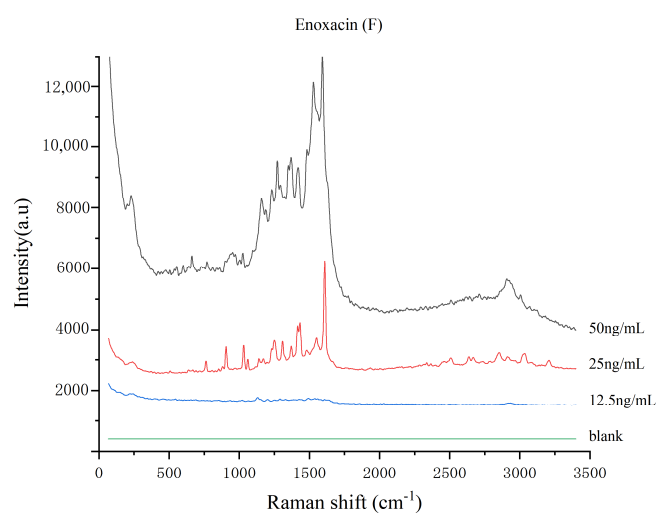


Figure S8. The SERS of the enoxacin (F) of different concentrations by the TLC-SERS.

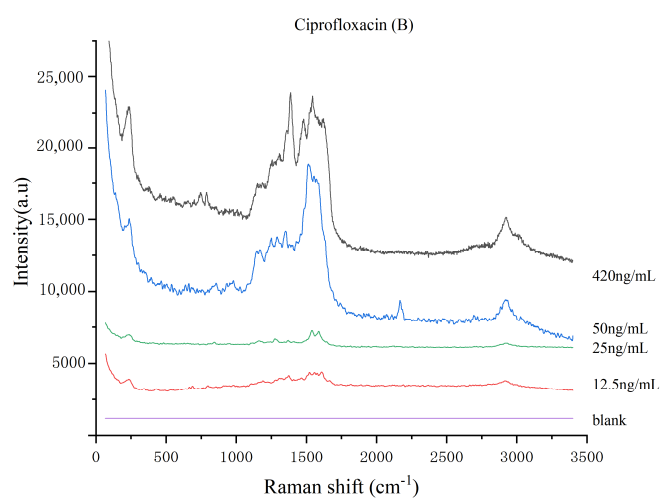


Figure S9. The SERS of the ciprofloxacin (B) of different concentrations by the TLC-SERS.

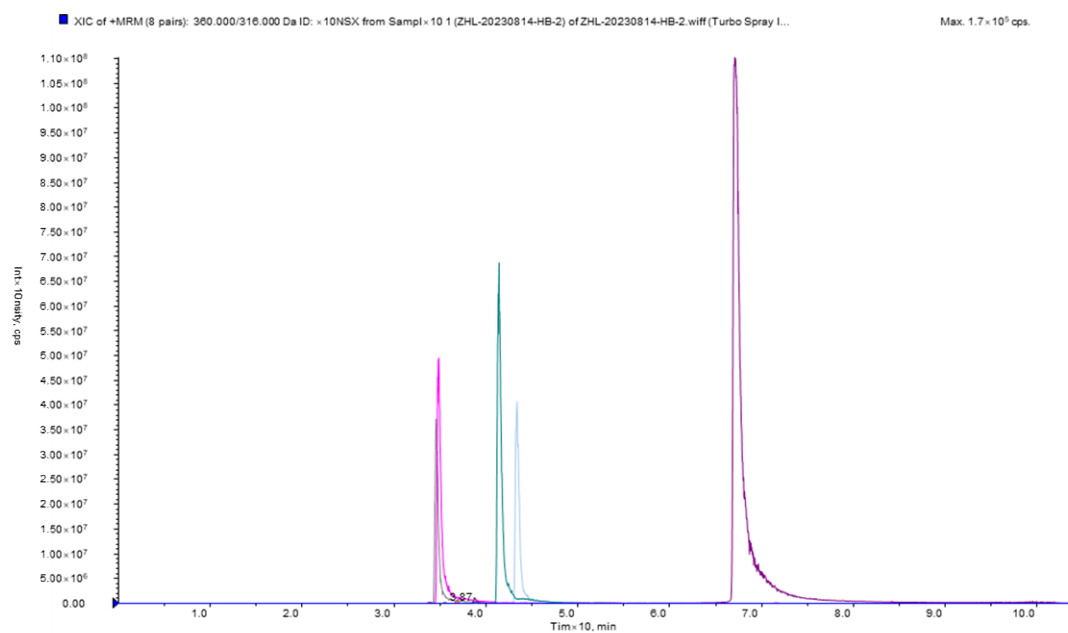


Figure S10. The ion flow chromatograms of eight quinolones.

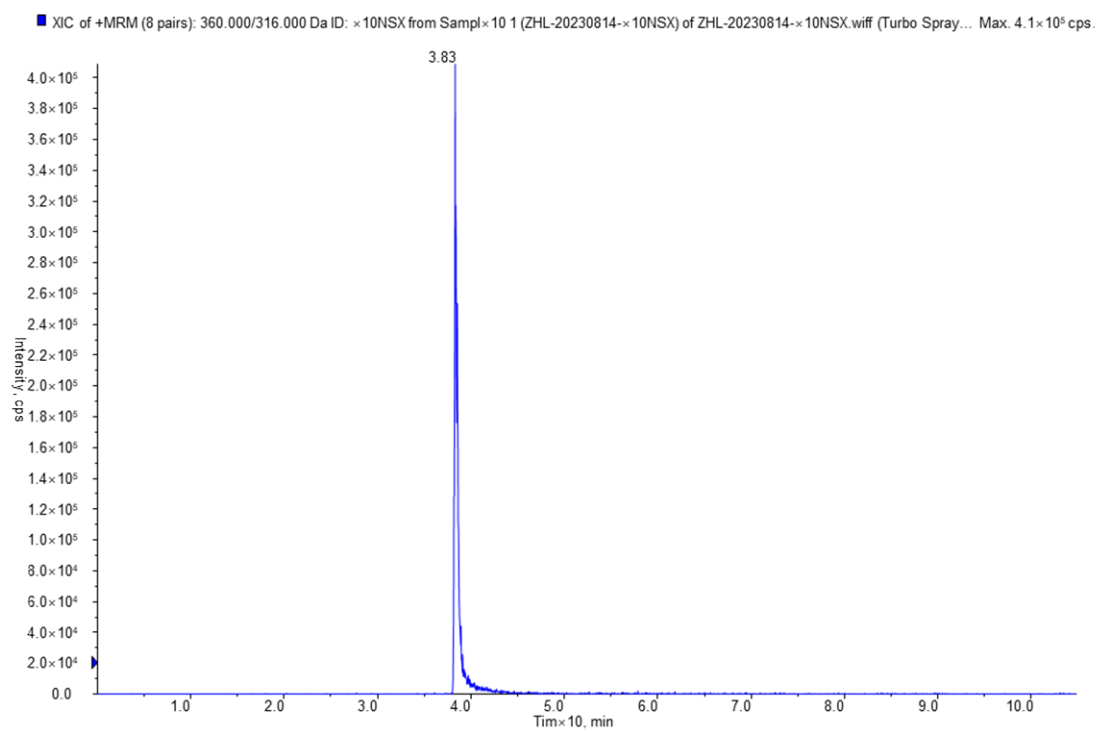


Figure S11. The chromatograms of sample 3 by UPLC-MS/MS.

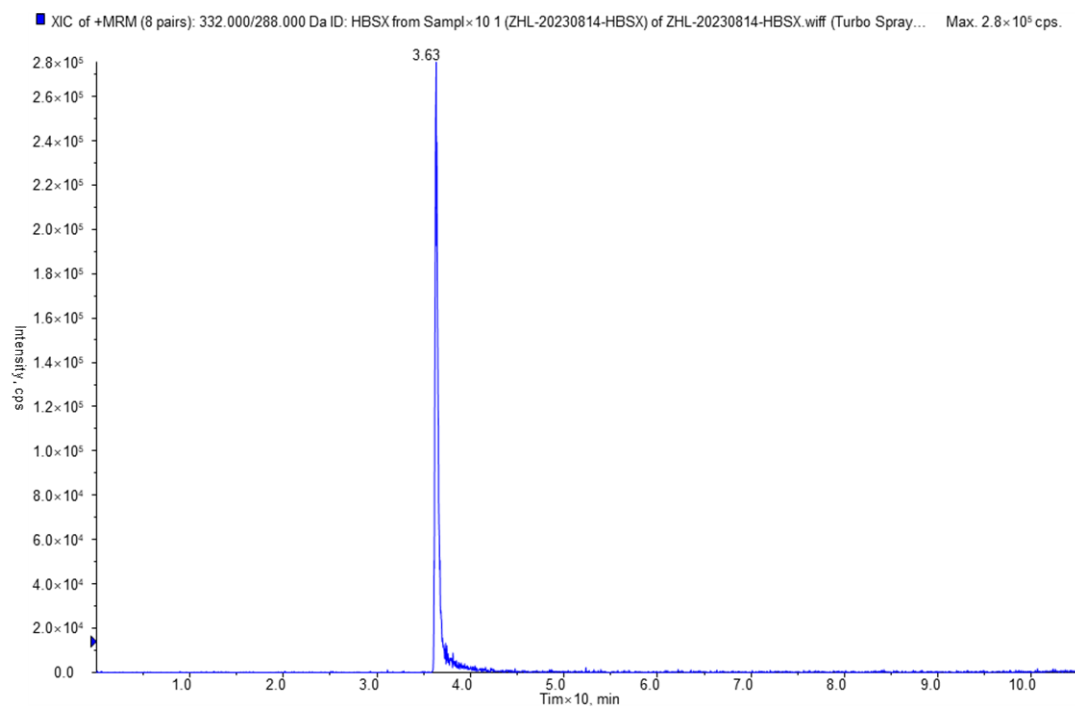


Figure S12. The chromatograms of sample 8 by UPLC-MS/MS.

Table S1. Comparison between the TLC-SERS and the UPLC-MS/MS to determine of the eight quinolones residues in aquatic products.

	UPLC-MS/MS			TLC-SERS		
	LOD ₁ (μg/kg)	RSD ₁ (%)	Time required (min)	LOD ₂ (μg/kg)	RSD ₂ (%)	Time required (min)
H	1.0	≤13.1	≅ 250	2.2	2.9~4.3	≅ 15
A	1.0	≤15.0	≅ 250	3.2	2.2~3.8	≅ 15
D	6.7	≤10.4	≅ 250	2.2	2.9~4.1	≅ 15
E	1.0	≤15.0	≅ 250	4.8	2.9~3.7	≅ 15
C	1.0	≤15.0	≅ 250	2.0	3.1~4.9	≅ 15
G	1.0	≤15.0	≅ 250	2.2	3.0~4.5	≅ 15
F	1.0	≤15.0	≅ 250	4.8	3.1~4.6	≅ 15
B	1.0	≤15.0	≅ 250	3.2	2.1~3.9	≅ 15

Under the UPLC-MS/MS, LOD₁ and RSD₁ are respectively the limit of detection and relative standard deviation Required by the National Standard of the People's Republic of China Announcement No. 1077-1-2008 of the Ministry of Agriculture. Under the TLC-SERS , LOD₂ is the actual limit of detection of the quinolones in the TLC-SERS; RSD₂ is the relative standard deviation of the S/N values at the characteristic peaks (v_{C-N}) from the quinolones reference materials of different concentrations. H, A, D, E, C, G, F, and B represent Nadifloxacin, Enrofloxacin, Fleroxacin, Sparfloxacin, Ofloxacin, Gatifloxacin, Enoxacin, and Ciprofloxacin, respectively.

Table S2. The EF at Raman spectra characteristic peaks of the eight quinolones.

	Functional group	Raman Shift (cm ⁻¹)	SERS				Raman			EF
			I _{SERS}	M _{SERS} (μg)	I _{SERS} /M _{SERS}	Raman Shift (cm ⁻¹)	I _{blank}	M _{blank} (μg)	I _{blank} /M _{blank}	
H	VC=C	1587	12896	2.0×10 ⁻⁴	6.4×10 ⁷	1620	562	10	56.2	1.1×10 ⁶
	VC=C	1398	12576	2.0×10 ⁻⁴	6.3×10 ⁷	1398	714	10	71.4	8.8×10 ⁵
	β _{CH2} , β _{CH3}	1257	8107	2.0×10 ⁻⁴	4.1×10 ⁷	1261	155	10	15.5	2.6×10 ⁶
	VC-N	1157	5509	2.0×10 ⁻⁴	2.8×10 ⁷	1136	196	10	19.6	1.4×10 ⁶
A	VC=C	1552	8131	4.0×10 ⁻³	2.0×10 ⁶	1628	655	10	65.5	3.1×10 ⁴
	VC=C	1389	7046	4.0×10 ⁻³	1.8×10 ⁶	1389	1577	10	157.7	1.1×10 ⁴
	β _{CH2} , β _{CH3}	1281	5385	4.0×10 ⁻³	1.3×10 ⁶	1284	100	10	10.0	1.3×10 ⁵
	VC-N	1173	4539	4.0×10 ⁻³	1.1×10 ⁶	1178	56	10	5.6	2.0×10 ⁵
D	VC=C	1535	14354	2.0×10 ⁻⁴	7.2×10 ⁷	1531	579	10	57.9	1.2×10 ⁶
	VC=C	1379	10803	2.0×10 ⁻⁴	5.4×10 ⁷	1381	1994	10	199.4	2.7×10 ⁵
	β _{CH2} , β _{CH3}	1298	8285	2.0×10 ⁻⁴	4.1×10 ⁷	1296	328	10	32.8	1.2×10 ⁶
	VC-N	1255	6650	2.0×10 ⁻⁴	3.3×10 ⁷	1227	520	10	52.0	6.3×10 ⁵
E	VC=C	1549	10418	2.0×10 ⁻⁴	5.2×10 ⁷	1533	758	10	75.8	6.9×10 ⁵
	VC=C	1373	7036	2.0×10 ⁻⁴	3.5×10 ⁷	1388	1977	10	197.7	1.8×10 ⁵
	β _{CH2} , β _{CH3}	1279	7215	2.0×10 ⁻⁴	3.6×10 ⁷	1286	3369	10	336.9	1.1×10 ⁵
	VC-N	1176	5145	2.0×10 ⁻⁴	2.6×10 ⁷	1176	543	10	54.3	4.8×10 ⁵
C	VC=C	1552	14493	8.0×10 ⁻⁵	1.8×10 ⁸	1554	460	10	46.0	4.0×10 ⁶
	VC=C	1394	12124	8.0×10 ⁻⁵	1.5×10 ⁸	1400	1488	10	148.8	1.0×10 ⁶
	β _{CH2} , β _{CH3}	1300	8055	8.0×10 ⁻⁵	1.0×10 ⁸	1300	170	10	17.0	5.9×10 ⁶
	VC-N	1151	6982	8.0×10 ⁻⁵	8.7×10 ⁷	1149	287	10	28.7	3.0×10 ⁶
G	VC=C	1562	14826	2.0×10 ⁻⁴	7.4×10 ⁷	1556	272	10	27.2	2.7×10 ⁶
	VC=C	1357	11110	2.0×10 ⁻⁴	5.6×10 ⁷	1371	232	10	23.2	2.4×10 ⁶
	β _{CH2} , β _{CH3}	1286	9437	2.0×10 ⁻⁴	4.7×10 ⁷	1280	154	10	15.4	3.1×10 ⁶
	VC-N	1151	7176	2.0×10 ⁻⁴	3.6×10 ⁷	1155	140	10	14.0	2.6×10 ⁶
F	VC=C	1540	8635	2.0×10 ⁻⁴	4.3×10 ⁷	1547	376	10	37.6	1.1×10 ⁶
	VC=C	1414	9081	2.0×10 ⁻⁴	4.5×10 ⁷	1404	4325	10	432.5	1.0×10 ⁵
	β _{CH2} , β _{CH3}	1265	5423	2.0×10 ⁻⁴	2.7×10 ⁷	1290	679	10	67.9	4.0×10 ⁵
	VC-N	1161	2942	2.0×10 ⁻⁴	1.5×10 ⁷	1153	144	10	14.4	1.0×10 ⁶
B	VC=C	1543	11656	4.0×10 ⁻³	2.9×10 ⁶	1570	414	10	41.4	7.0×10 ⁴
	VC=C	1386	11892	4.0×10 ⁻³	3.0×10 ⁶	1387	3036	10	303.6	9.9×10 ³
	β _{CH2} , β _{CH3}	1307	7613	4.0×10 ⁻³	1.9×10 ⁶	1313	332	10	33.2	5.7×10 ⁴
	VC-N	1151	5472	4.0×10 ⁻³	1.4×10 ⁶	1162	145	10	14.5	9.6×10 ⁴

EF is the Raman enhancement factor, I_{SERS} and I_{blank} are the Raman intensities at characteristic peaks of the SERS active substrate and blank substrate; M_{SERS} and M_{blank} are the mass (μg) of the quinolones on the SERS active substrate and blank substrate. H, A, D, E, C, G, F, and B represent Nadifloxacin, Enrofloxacin, Fleroxacin, Sparfloxacin, Ofloxacin, Gatifloxacin, Enoxacin, and Ciprofloxacin, respectively.