Electronic Supplementary Information

High efficiency screening of nine lipid-lowering adulterants in herbal dietary supplements by using thin layer chromatography coupled with surface enhanced Raman spectroscopy

Qingxia Zhu [1] · Mengyun Chen [2] · Lu Han [1] · Yongfang Yuan [1,*] · Feng Lu [2,]**

[1] Department of Pharmacy, Shanghai Ninth People's Hospital, Shanghai JiaoTong University School of Medicine, Shanghai, 201999, China.
[2] Department of Pharmaceutical Analysis, School of Pharmacy, Second Military Medical University, Shanghai, 200433, China.

* Corresponding author. E-mail addresses: nmxyyf@126.com (Y. Yuan)

** Corresponding author. E-mail addresses: fenglufeng@hotmail.com (F. Lu).

Qingxia Zhu and Mengyun Chen contributed equally to this work.

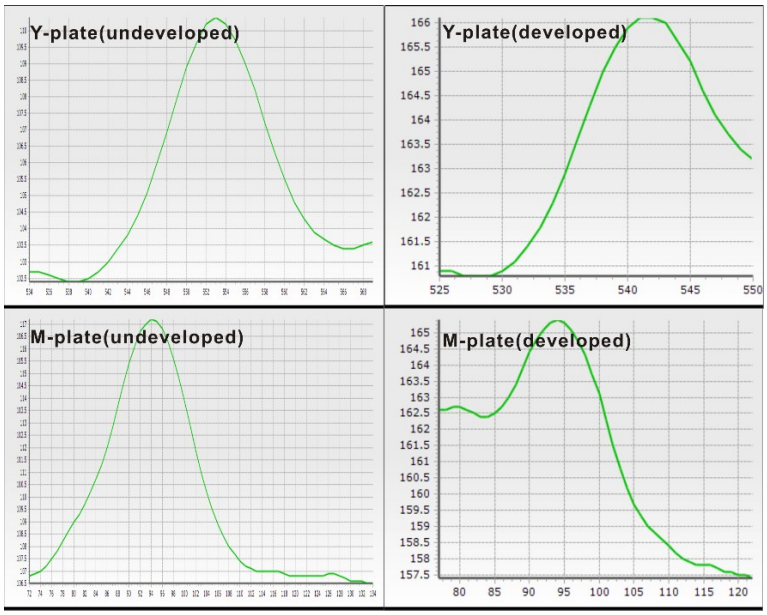

Fig. S1. The chromatographic peaks of undeveloped and developed spots on different TLC plates.

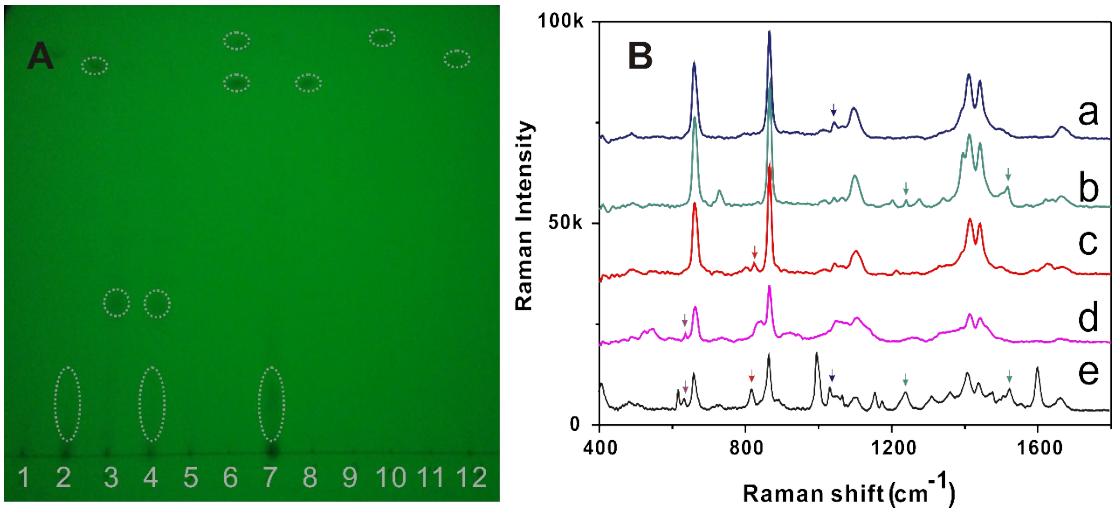

Fig. S2. (A) The TLC image of HDS matrix developed by dichloromethane-methanol-water 8:2:0.2 (*v/v*) and (B) the SERS spectra of matrix (a-d) and ATO (e).

Fig. S3. The TLC image of HDS matrix developed by petroleum ether-acetic ether - acetic acid 5.5:2.8:1(*v/v*).

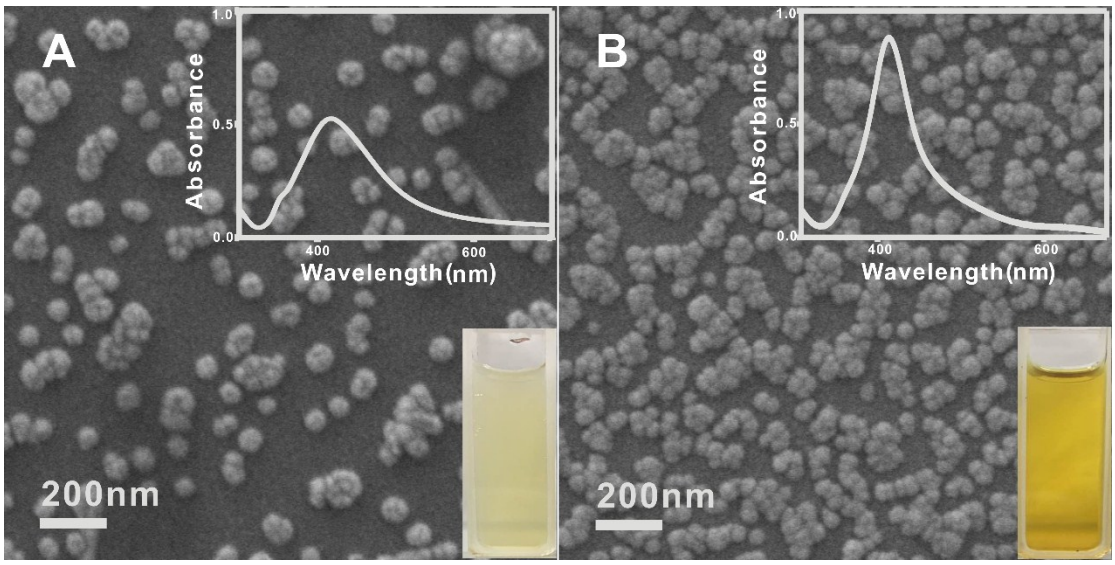

Fig. S4. UV-vis spectra and SEM image of the prepared silver colloids: (A) L-colloids and (B) D-colloids. The inset shows the accompanying color of the prepared silver colloids.

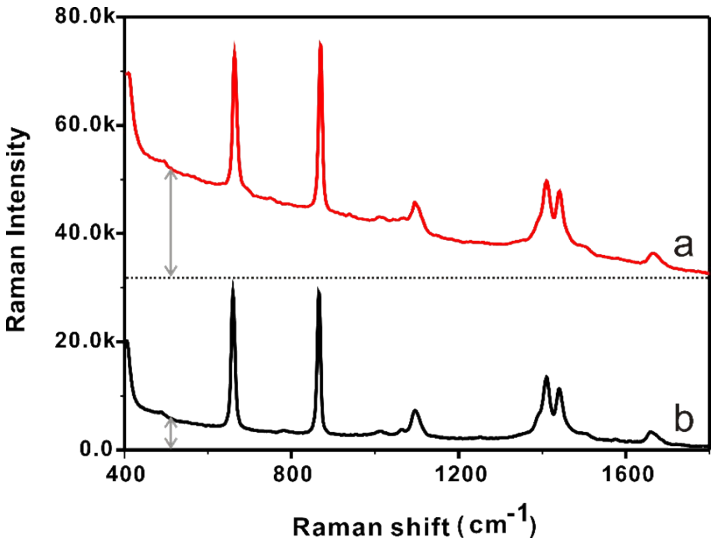

Fig. S5. The fluorescence interference from different HPTLC plates: (a) Y-plate and (b) M-plate.

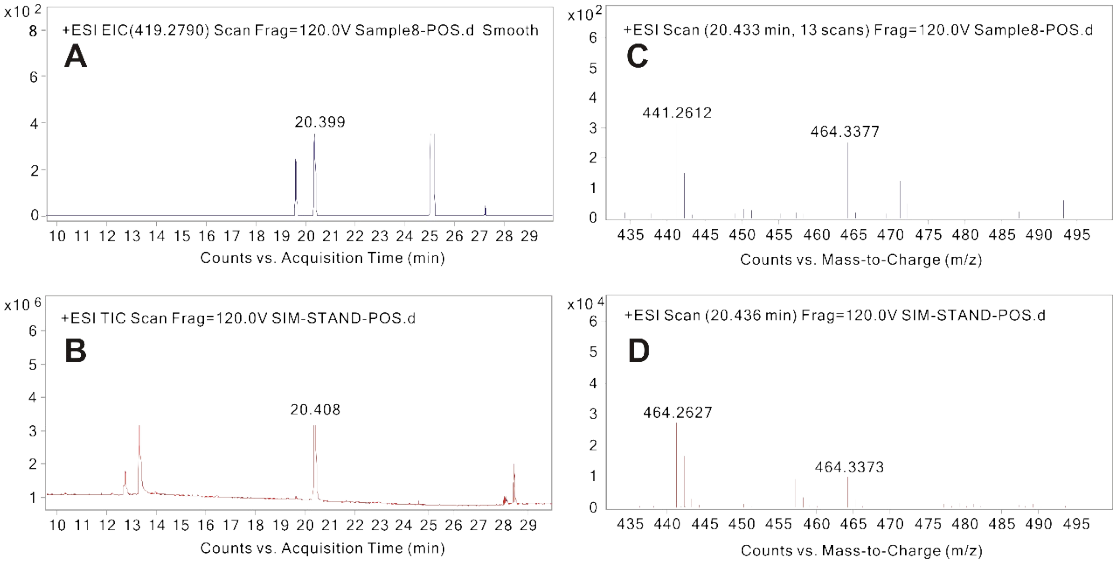

Fig. S6. HPLC spectra of (A) sample 8 and (B) standards of SIM; MS spectra of (C) sample 8 and standard of (D) SIM.

LC-MS verification conditions: ACQUITY UPLCTM BEH C18 column (2.1 mm× 100 mm, 1.7m, Waters, Milford, MA) was used with a mobile-phase gradient prepared from formic acid (component A) and 0.1% formic acid in acetonitrile (component B). The gradient was: held at 5% B for 2 min, linear increase from 5-25% B in 7 min, linear increase from 25-55% B in 11 min, linear increase from 60-95% B in 3 min, and held at 95 % B for 2 min. The flow rate was 0.35 mL/min, the injection volume was 4 μL, and the column temperature was 40℃. The following MS conditions were applied: ion source was the ESI source, using the positive ion mode (detection of PRO with negative ion mode). MS scanning range was from 100 to 1100 m/z.

Table S1 LOD comparison of six analytes by LC-MS/MS method and TLC-SERS method (unit: μg).

	NIC	PRA	ATO	FLU	BEZ	SIM	FEN
LC-MS/MS	0.02	0.012	0.004	0.004	0.02	0.002	0.002
TLC-SERS	0.0025	0.01	0.0025	0.01	0.001	0.05	0.005

Table S2 Validation of SIM in sample 8 by UPLC-QTOF/MS.

Name	**Identification formula** $[M+H]^+$	**Mass**	**Error (ppm)**
SIM standard	$C_{25}H_{38}O_5$	418.5719	-0.38
Sample 8	$C_{25}H_{38}O_5$	418.5714	-0.12