

Rapid, accurate, and quantitative detection of propranolol in multiple human biofluids *via* surface-enhanced Raman scattering

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Table S1 LC-MS solvent gradient for reverse phase analysis

Time (min)	Flow Rate ($\mu\text{L min}^{-1}$)	Mobile Phase A ($\text{H}_2\text{O}\%$)	Mobile Phase B ($\text{MeOH}\%$)
0	400	80	20
1	400	80	20
4	400	5	95
6	400	5	95
7	400	80	20

Table S2 Assignments of serum peaks labelled in Figure 2. ¹⁻³

Band (cm^{-1})	Vibrational mode	Assignment
632	C–S stretch	Tyrosine
723	C–H bending	Adenine
810	Ring breathing	Tyrosine
959	C–C	α -Helix, proline, valine
1096	C–N	D-Mannose
1132	C–N	D-Mannose
1204	Ring vibration	Phenylalanine, tryptophan
1330	—	Amide III
1446	CH_2 bending	Collagen, lipids
1583	—	Tryptophan, phenylalanine
1696	—	Amide I

Table S3 Assignments of plasma peaks labelled in Figure 2. ^{3,4}

Band (cm⁻¹)	Vibrational mode	Assignment
491	Ring vibration	Cellulose, guanine, L-arginine
590	—	Ascorbic acid, amide-VI
634	C-S	L-Tyrosine,
725	C-H	Adenine
810	C-C-O	L-Serine, glutathione
885	C-O-H	Glutathione, D-(C)-galactosamine
1012	C-C	Phenylalanine
1074	C-N	Collagen
1132	C-N	D-Mannose
1209	Ring vibration	L-Tryptophan, phenylalanine
1358	—	Tryptophan, adenine, guanine
1448	CH ₂	Collagen, phospholipids
1580	C-C	Phenylalanine, acetoacetate, riboflavin
1684	C=O	α -Helix, collagen

Table S4 Assignments of urine peaks labelled in Figure 2. ⁵⁻⁸

Band (cm⁻¹)	Vibrational mode	Assignment
658	C=O-N deformation	Uric acid
713	C-H stretching	Hypoxanthine
804	C-C stretching	Amino acid
1002	C-N stretching	Phenylalanine
1133	C-N stretching	Uric acid
1218	Ring vibration	Phenylalanine
1350	C-H deformation	Adenine
1448	—	Tryptophan
1582	ring stretches	Phenylalanine

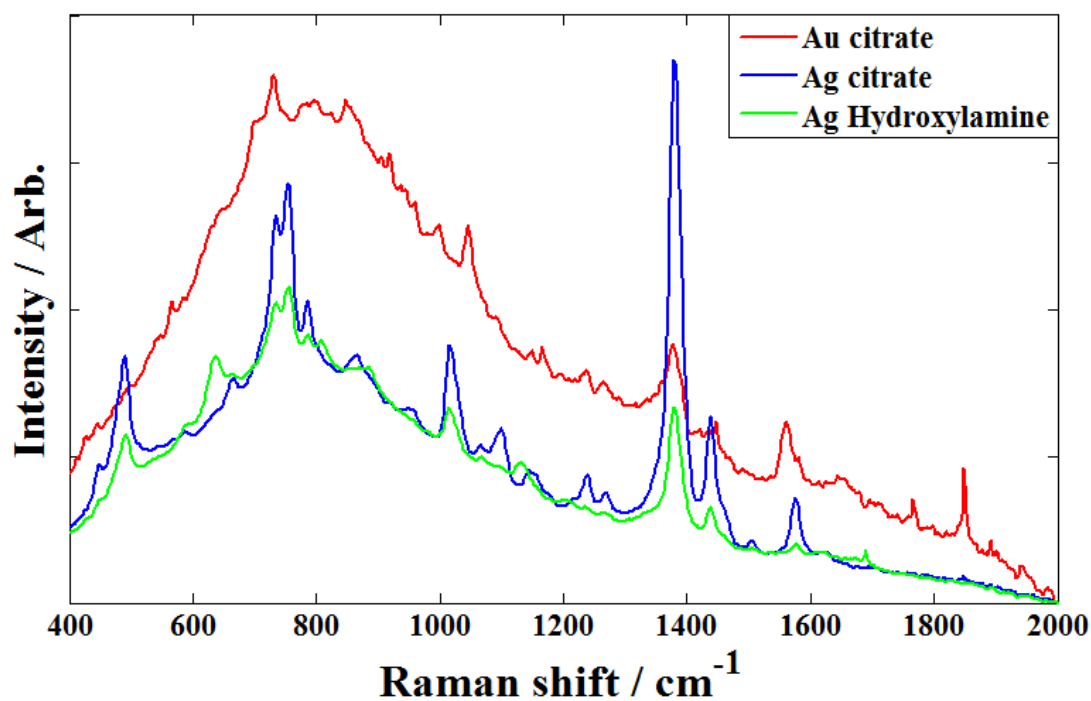


Figure S1 Plot shows SERS spectra of using different nanoparticles (Au citrate, Ag citrate and Ag hydroxylamine) in conjunction with 200 μM of propranolol spiked into filtered plasma.

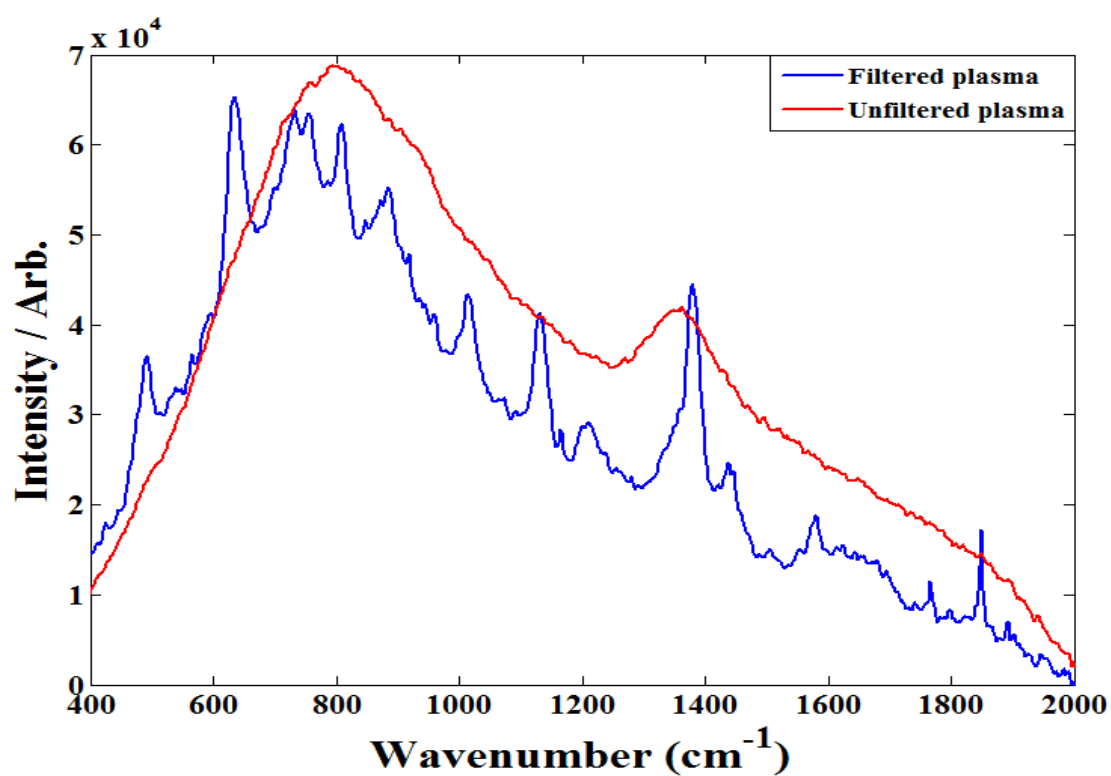


Figure S2 Plot shows SERS spectra of filtered and unfiltered plasma spiked with 0.5 mM propranolol.

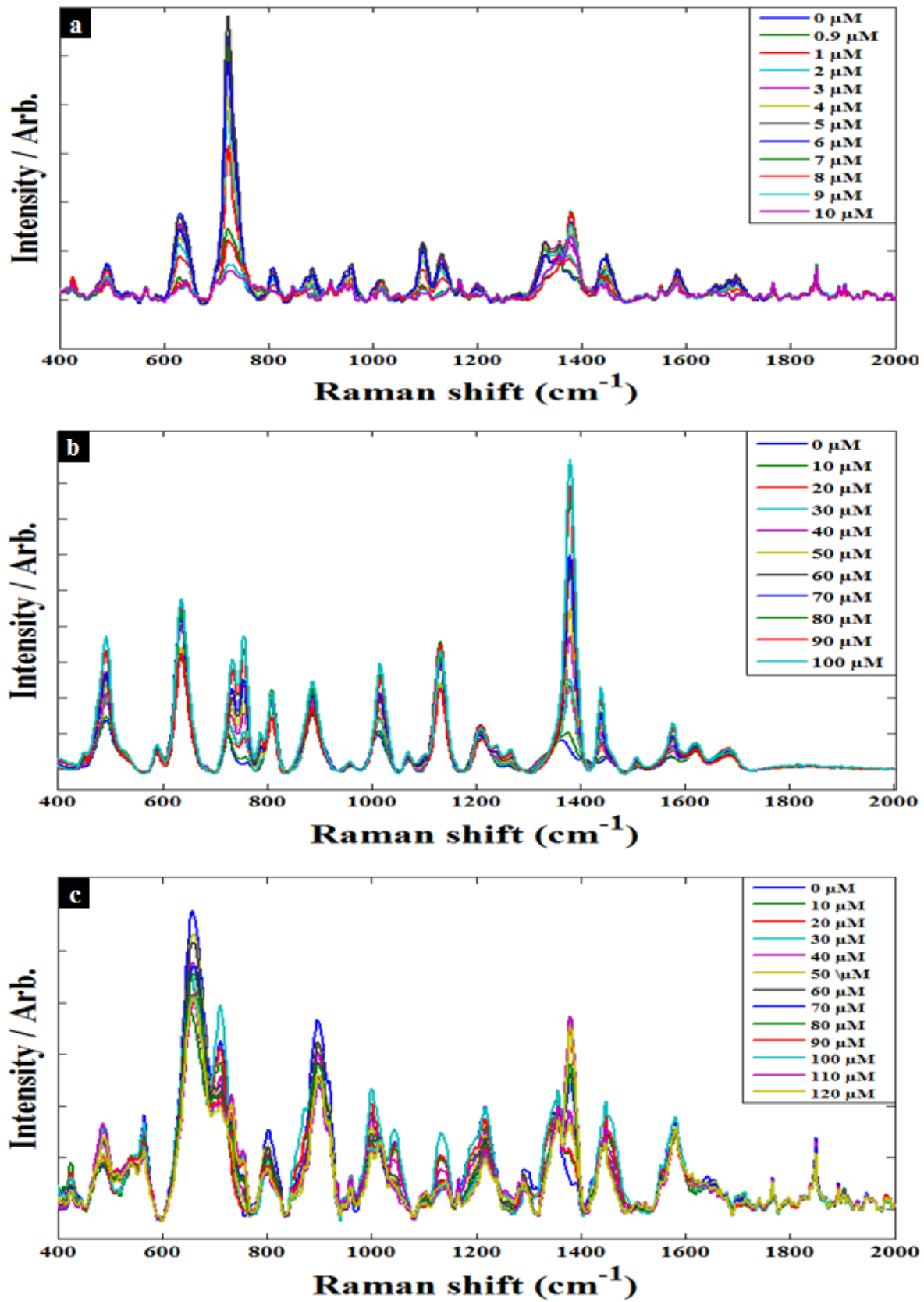


Figure S3. SERS spectra illustrate the different concentrations of propranolol spiked into biofluids: (a) serum, (b) plasma, and (c) urine

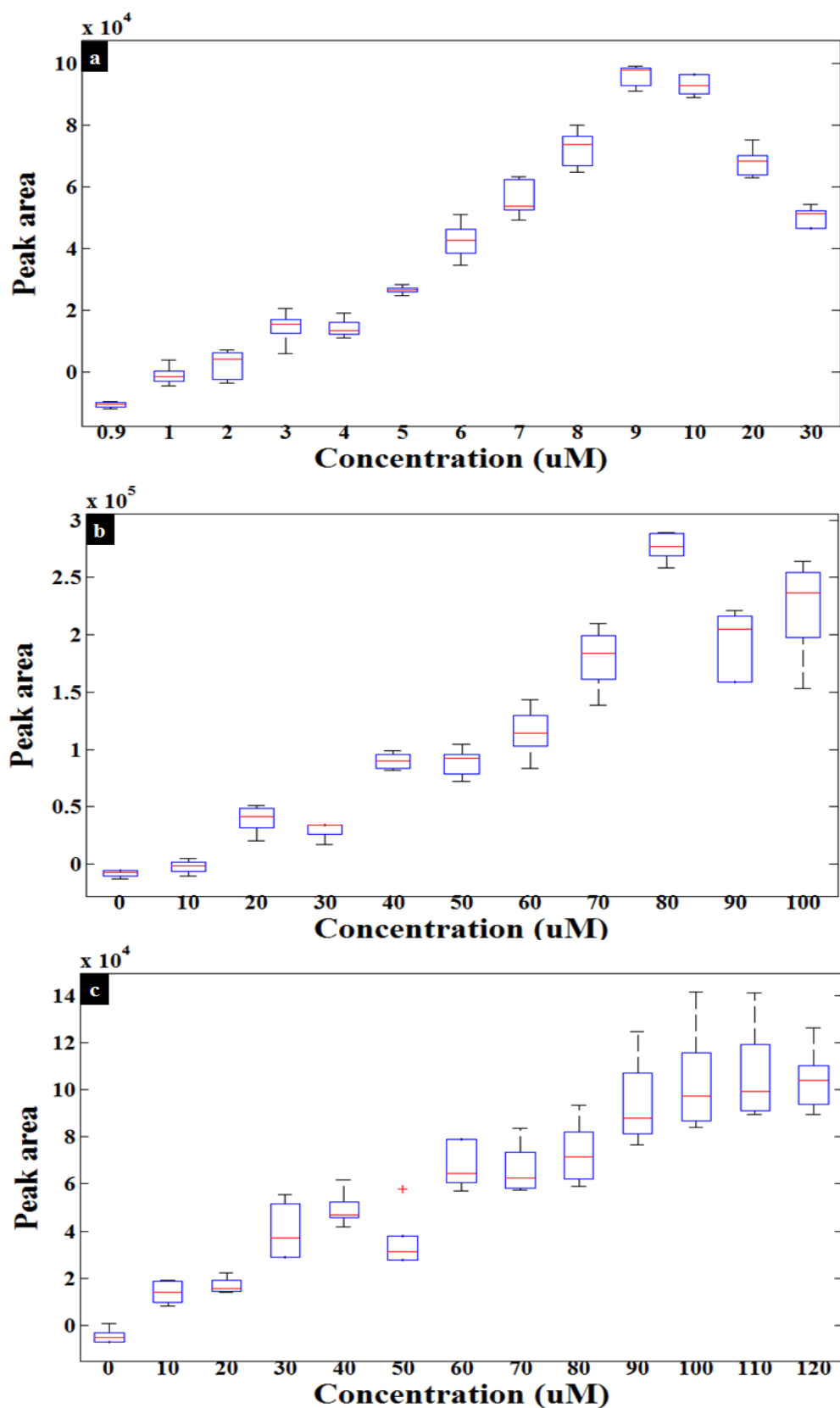


Figure S4. Box and Whisker plots of the area under the peak at 1381 cm^{-1} versus propranolol concentrations spiked into the following human biofluids: (a) serum, (b) plasma, and (c) urine. These data are from five replicates where the red line represents the median value, the blue box the interquartile range, the error bars the 95% confidence region and the red crosses any outliers. Note in (a & c) that the x-axis is not plotted to scale.

SERS of propranolol spiked in plasma *before* the pre-filtration step

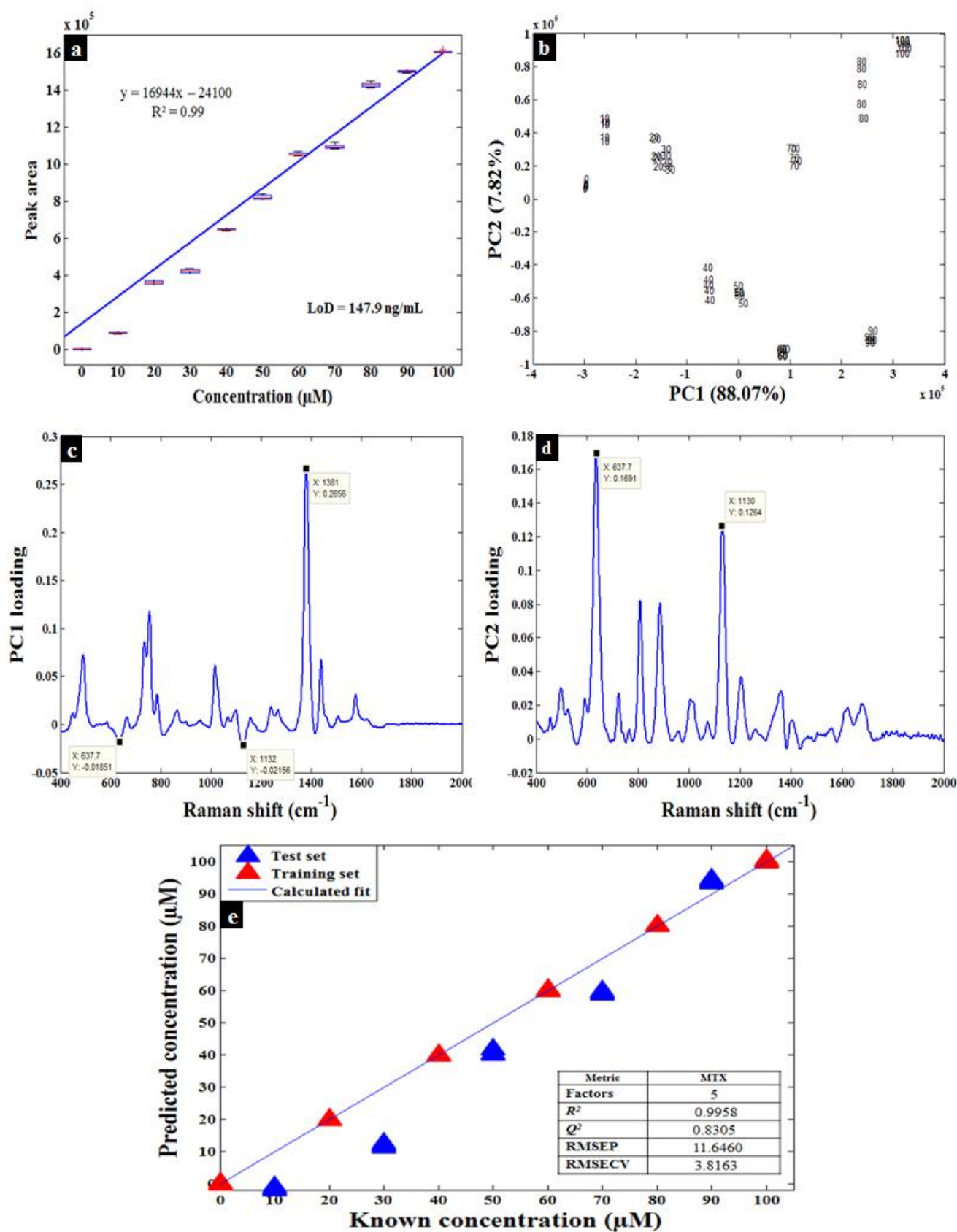


Figure S5. (a) Plot of the area under the peak at 1381 cm^{-1} versus propranolol concentrations spiked into plasma *before* filtration. (b) PCA and loadings plots of (c) PC1 and (d) PC2. (e) PLSR

SERS of propranolol spiked in plasma *after* the pre-filtration step

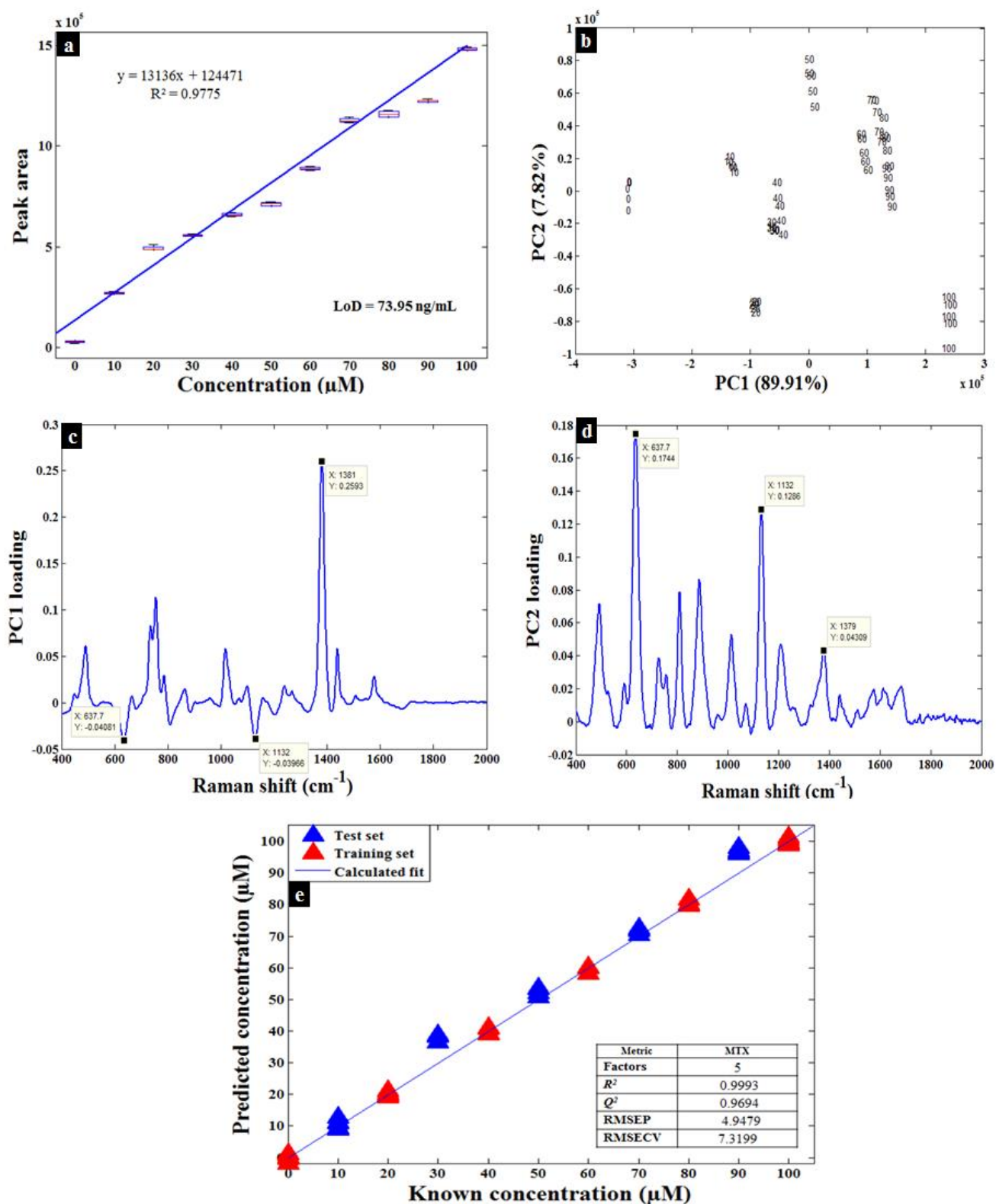


Figure S6. (a) Plot of the area under the peak at 1381 cm^{-1} versus propranolol concentrations spiked into plasma after filtration. (b) PCA and loadings plots of (c) PC1 and (d) PC2. (e) PLSR

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