Supporting Information

for

"Magnetic solid phase extraction coupled with desorption corona beam ionization – mass spectrometry for rapid analysis of antidepressants in human body fluids"

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LC-UV conditions. The LC-UV experiment was performed on a LC-20A system (Shimadzu, Japan) which consists of binary LC-20AD pumps, a DGU-20A3 degasser, and a SPD-20AC column oven. The analytical column was a HiSep C18 column (250 mm× 4.6 mm i.d., 5 μm; Weltech, Wuhan, China). The mobile phase consisted of 25 mM phosphate buffer (pH 3.8)/ACN (44:56, v/v), and the flow rate was maintained at 1 mL/min. The column temperature was set at 40 °C. The UV detection was 230 nm and the sample injection volume was 20 μL.

Investigation of the batch-to-batch reproducibility of Fe_3O_4@Ppy. Coupled with Fe_3O_4@Ppy-based MSPE, liquid chromatography-ultraviolet (LC-UV) was applied to verify the reproducibility of antidepressant quantitation using different batches of nanoparticles. Three batches of Fe_3O_4@Ppy prepared under the same conditions were used for extraction of antidepressants in standard solutions. The extraction conditions were modified from the optimized MSPE conditions described previously in this study. Solvent desorption was applied, and desorption process was optimized to ensure complete desorption of the target analytes from the magnetic sorbents. The typical procedure was summarized as follows: 20 mg of Fe_3O_4@Ppy was put into an 8 mL vial and then 5 mL of phosphate buffer (25 mM, pH 7.0) spiked with antidepressants (200 ng/mL for each analyte). After vortexing for 3 min, the magnetic particles were magnetically separated from the solution with the assistance of a magnet and then washed with 3 mL of H_2O for 3 min. After the washing solution was discarded, antidepressants were desorbed from magnetic particles with 2 mL of acetone (containing 1.0% formic acid) under vortex (3 min). The solution was separated from Fe_3O_4@Ppy by a magnet and collected in a vial. Then, the solution was evaporated to dryness

under a mild nitrogen stream at room temperature. The residue was dissolved in 100 μL of mobile phase, and 20 μL of the solution was analyzed by LC-UV.

Evaluation of recoveries of three antidepressants in different matrix. To study the effect of biologically relevant impurities on Fe_3O_4@Ppy-based extraction, extraction efficiencies in different matrix were studied by MSPE-LC-UV. The extraction conditions were the same as the optimized MSPE conditions described previously in this study. Solvent desorption was applied, and desorption process was optimized to ensure complete desorption of the target analytes from the magnetic sorbents. The typical procedure was as follows: Fe_3O_4@Ppy suspension (10 μL, 0.1 mg Fe_3O_4@Ppy) was added into 1 mL of standard solution (25 mM phosphate buffer, pH 7.0), urine sample (diluted 5 times with phosphate buffer (25 mM, pH 7.0)) or plasma sample (diluted 10 times with phosphate buffer (25 mM, pH 7.0)) spiked with antidepressants (200 ng/mL for the final solution). After vortexing for 0.5 min, the magnetic material was magnetically gathered to the vial bottom with the assistance of an external magnet and then washed with 1 mL of H_2O for 0.5 min. After the washing solution was discarded, antidepressants were desorbed from magnetic particles with 1 mL of acetone (containing 1.0% formic acid) under vortex (3 min). Then, the solution was evaporated to dryness under a mild nitrogen stream at room temperature. The residue was dissolved in 100 μL of ACN, and 20 μL of the solution was supplied to LC-UV for analysis.

Evaluation of analyte losses in each step of MSPE. Coupled with LC-UV detection, analyte losses in each step of MSPE were evaluated. The typical procedure was as follows: Fe_3O_4@Ppy suspension (10 μL, 0.1 mg Fe_3O_4@Ppy) was added into 1 mL of standard solution spiked with antidepressants (200 ng/mL for each analyte). After vortexing for 0.5

min, the magnetic material was magnetically gathered to the vial bottom with the assistance of an external magnet. The solutions were collected and lyophilized to dryness. The residue was dissolved in 100 μL of ACN, and 20 μL of the solution was supplied to LC-UV for analysis. The percentages of analytes retained in washing solution was detected in the same way.

Table S1. SRM transitions at different collision energies for each analyte.

Analyte	SRM transitions(m/z)	Collision energy(eV)
Citalopram	325.2→109.1 [a]	30
	325.2→262.2	20
Sertraline	306.1→159.0 [a]	26
	306.1→275.1	13
Fluoxetine	310.1→44.2 [a]	14
	310.1→148.2	9
Chlorphenamine	275.0→230.1 [a]	16
	275.0→167.2	39

a, Transition monitored for quantitative analysis.

Table S2. Extraction response signal and RSD value of antidepressants with three different batches of Fe_3O_4@Ppy (Standard solutions spiked with antidepressants at the concentration of 200 ng/mL).

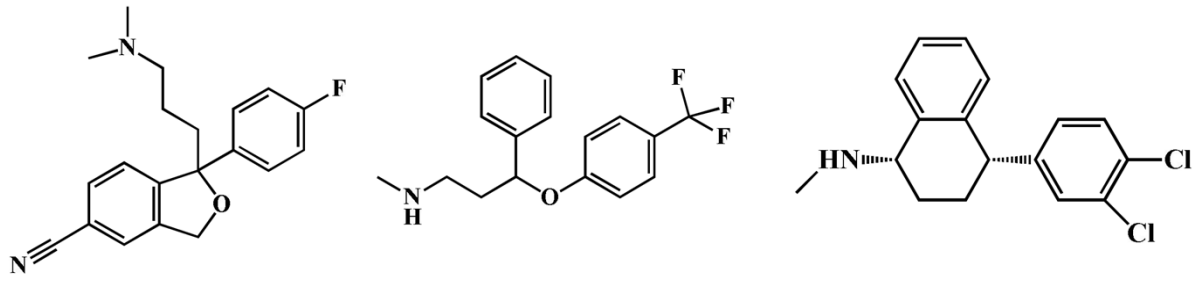
Analyte	Response			RSDs (%)
	batch 1	batch 2	batch 3	
Citalopram	187735	183003	197137	3.8
Sertraline	168584	178723	183730	4.4
Fluoxetine	205673	214502	224514	4.4

Table S3. Calibration curves and LODs of antidepressants obtained by MSPE-DCBI-MS method.

Sample	Compounds	Linear range (μg/mL)	Regression line		r^2	LOD (ng/mL)
			a	B		
Urine	Citalopram	0.005-0.5	2.917±0.271	0.271±0.020	0.951	1.0
	Sertraline	0.005-0.5	22.099±1.438	-0.047±0.016	0.975	0.2
	Fluoxetine	0.005-0.5	5.999±0.343	0.002±0.005	0.981	0.5
Plasma	Citalopram	0.02-1	2.631±0.203	0.0770.083	0.971	5
	Sertraline	0.02-1	8.254±0.597	0.358±0.057	0.974	2
	Fluoxetine	0.02-1	3.111±0.281	0.175±0.031	0.960	5

Table S4. Recoveries of three antidepressants obtained by MSPE-DCBI-MS method.

Sample	Compound	Added (μg/mL)	Recovery (%)	RSDs (n=5, %)
Urine	Citalopram	0.01	108.5	19.1
		0.05	109.2	12.6
		0.2	115.1	13.7
	Sertraline	0.01	100.6	14.9
		0.05	101.7	13.3
		0.2	112.4	14.5
	Fluoxetine	0.01	103.1	15.8
		0.05	109.1	16.5
		0.2	118.7	12.6
Plasma	Citalopram	0.05	88.2	18.3
		0.2	106.9	16.1
		0.5	99.9	15.4
	Sertraline	0.05	85.2	14.8
		0.2	104.5	18.2
		0.5	102.7	17.3
	Fluoxetine	0.05	86.4	16.9
		0.2	98.0	14.5
		0.5	95.1	15.7



Citalopram Fluoxetine Sertraline

Fig. S1. The chemical structures of three antidepressants.

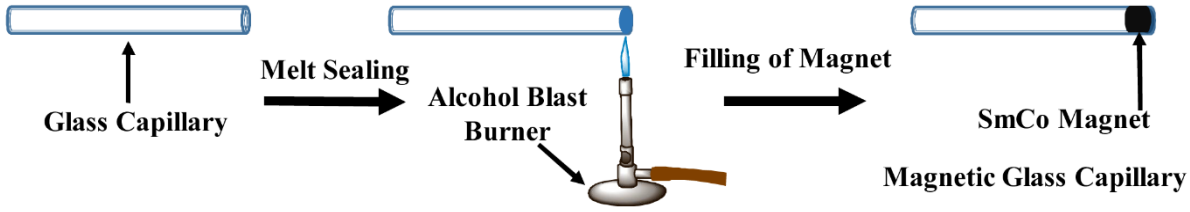


Fig. S2. Schematic diagram for the construction of magnetic glass capillary.

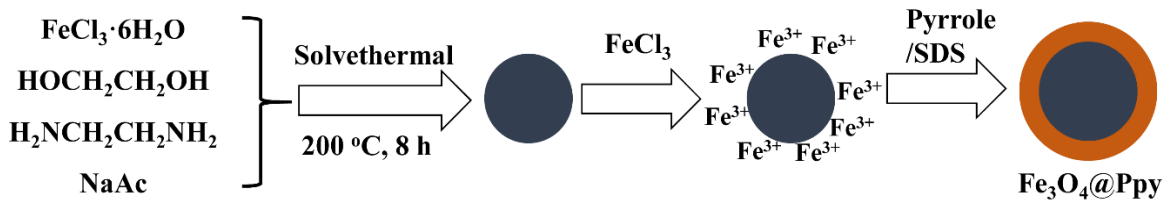


Fig. S3. Preparation scheme of Fe_3O_4@Ppy.

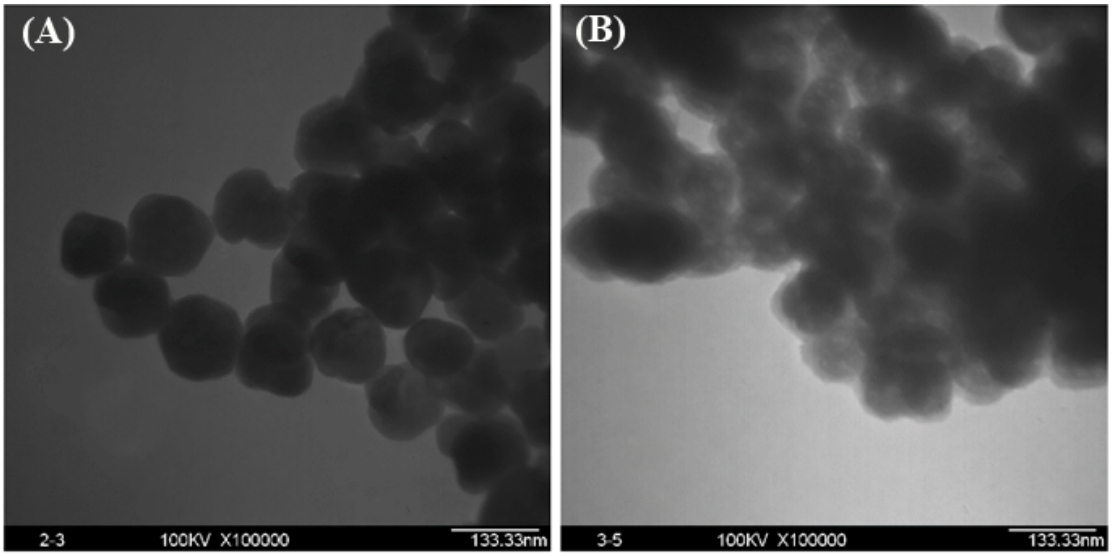


Fig. S4. TEM images of Fe_3O_4 (A) and Fe_3O_4@Ppy (B).

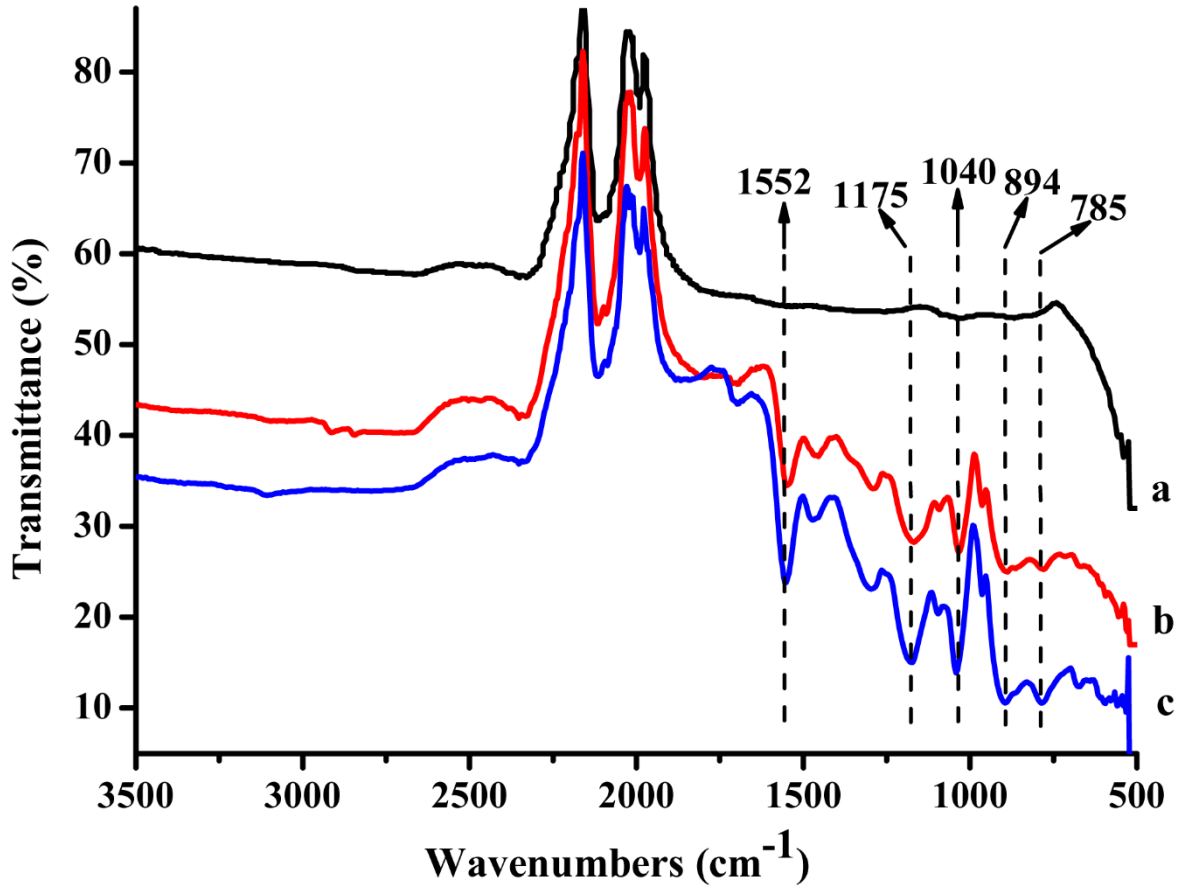


Fig. S5. IR spectra of Fe_3O_4 (a), Fe_3O_4@Ppy (b) and Ppy (c).

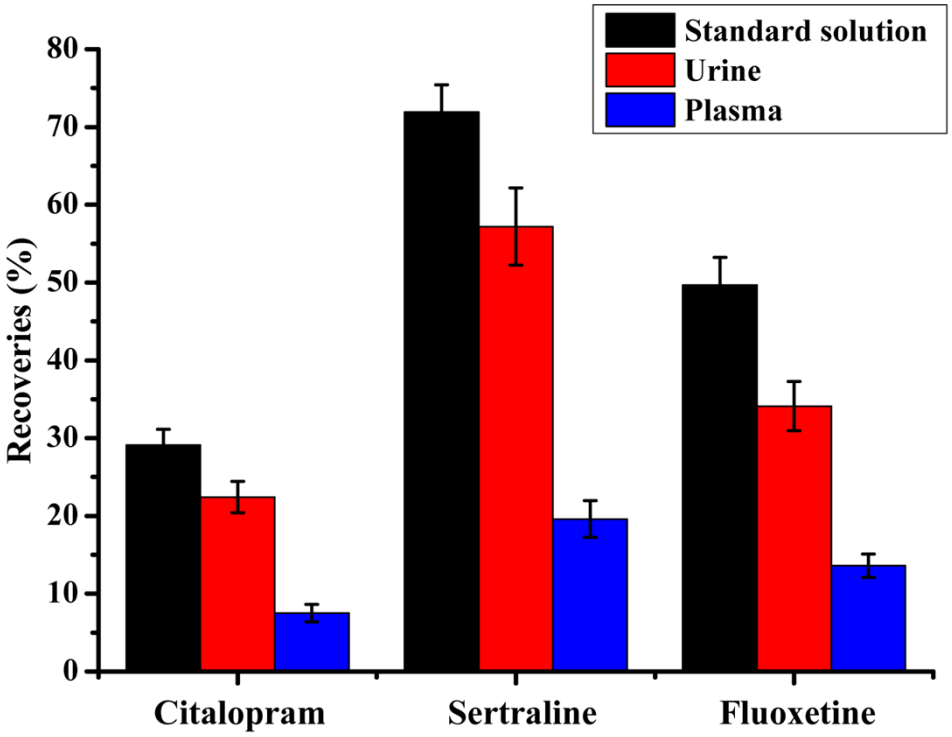


Fig. S6. Recoveries of three analytes in standard solution, urine sample and plasma sample.

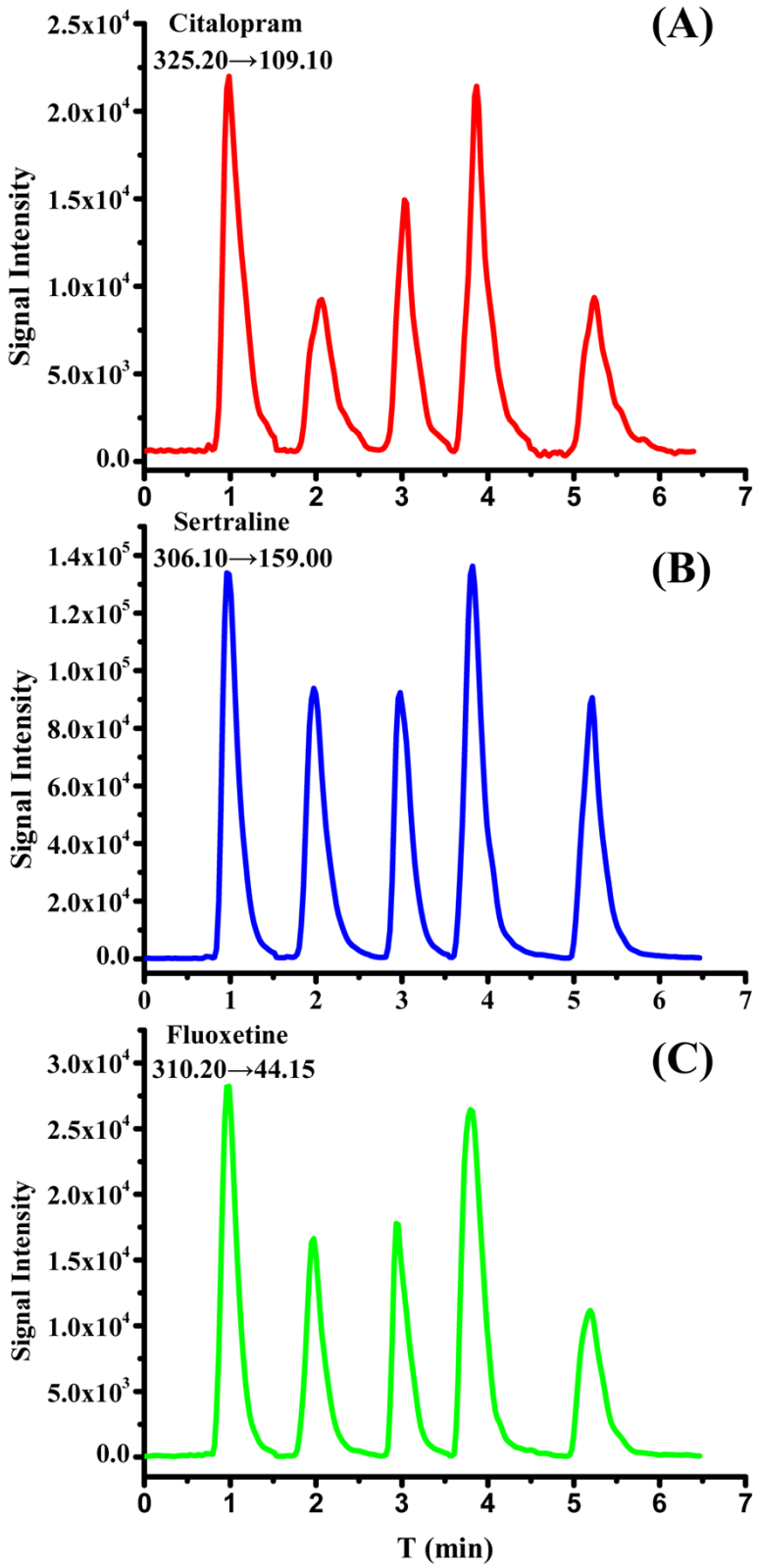


Fig. S7. Typical MS spectra of three antidepressants in urine sample spiked with 500 ng/mL of antidepressants. Analyses were performed continuously for five runs and detected in SRM mode.

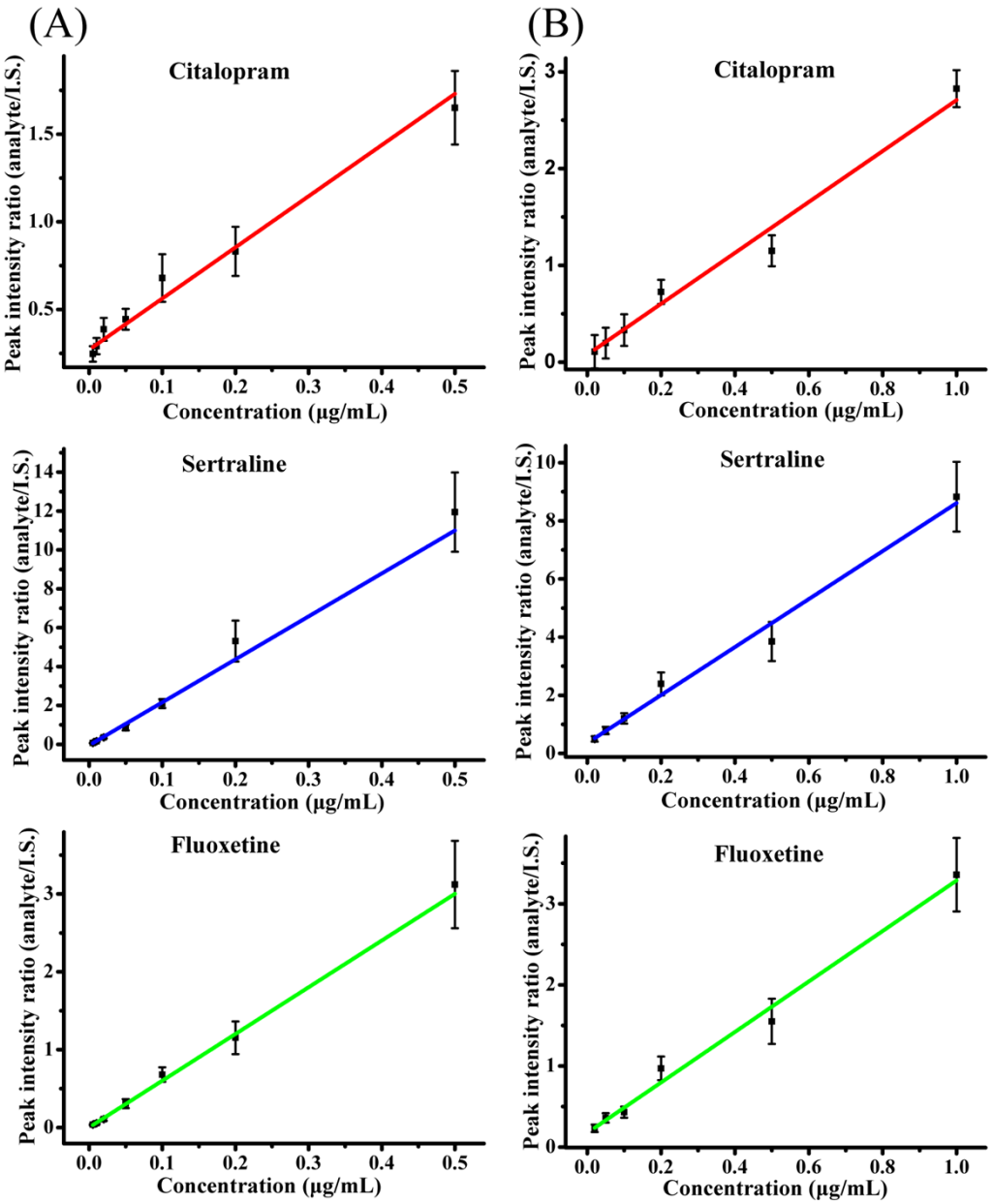


Fig. S8. Calibration curves of three antidepressants in (A) urine and (B) plasma.