Electronic Supporting Information (ESI)

A twin enrichment method based on dispersive liquid-liquid microextraction and field-amplified sample injection for the simultaneous determination of sulfonamides

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Bernoulli equation

$$u = \frac{\Delta P \cdot r^2}{8\eta L}$$

$\Delta P = 3.45kPa$, r is the capillary radius, η is the viscosity of water, L is the effective length of the capillary. The experimental results were shown in Fig. 3A. When the water plug length is 0.507 cm (3.45 kPa × 3 s), the enrichment efficiency of the four SAs reaches the maximum. When the water injection time is less than 3 s, the subject to be measured will be rapidly pushed out of the capillary tube by electric seepage, and the detection sensitivity of the analytes cannot be greatly improved. When the water injection time is longer than 3 s, serious peak broadening and overlap will occur. Therefore, the optimum length of water plug is 0.507 cm.

Fig. S1 Molecular structures of the four SAs analyzed in this work.

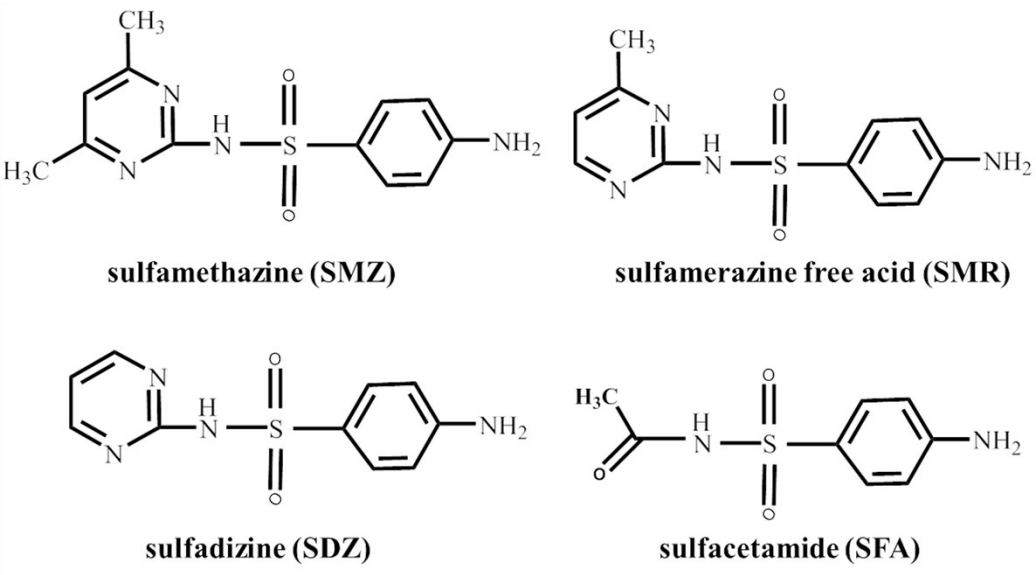

Fig. S2 Effect of NaH_2PO_4 concentration on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

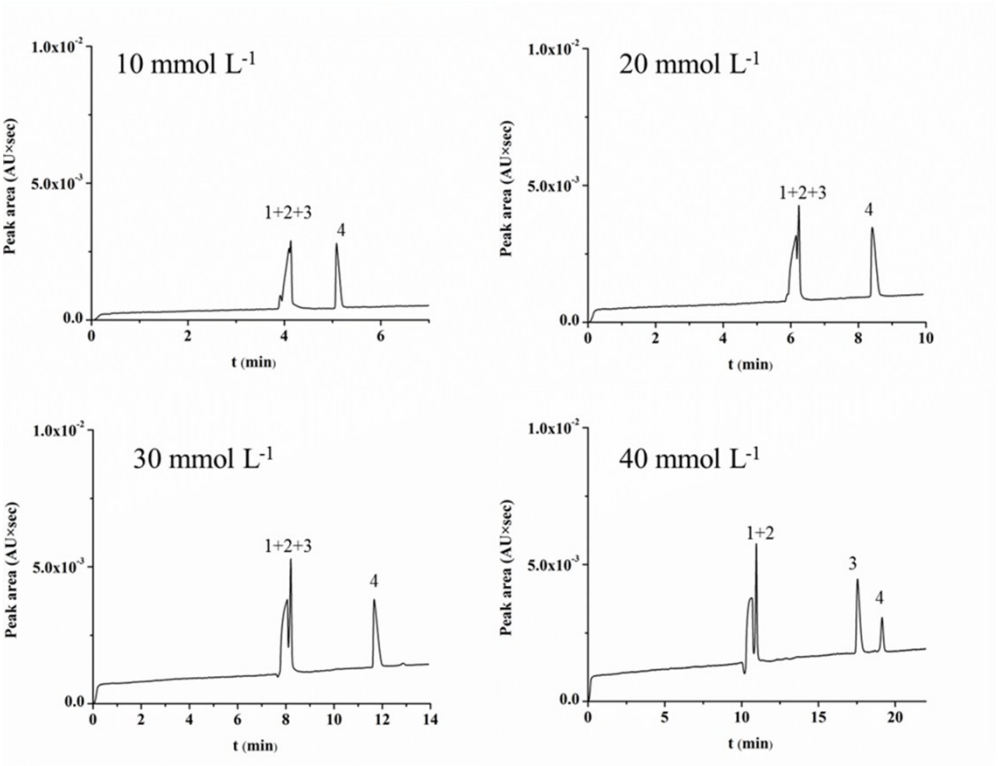

Fig. S3 Effect of buffer pH on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

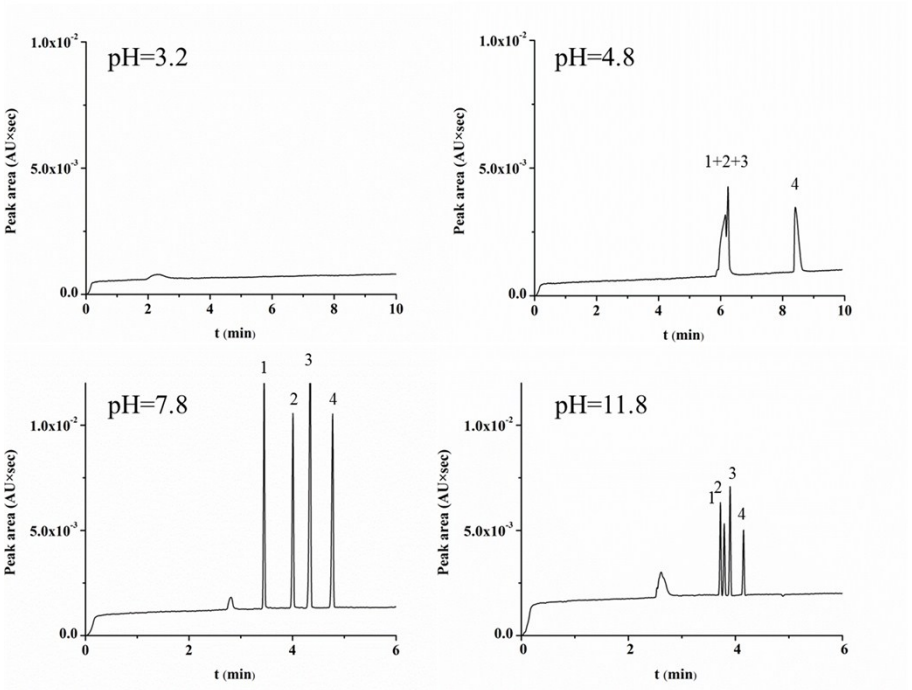

Fig. S4 Effect of MeOH and ACN on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

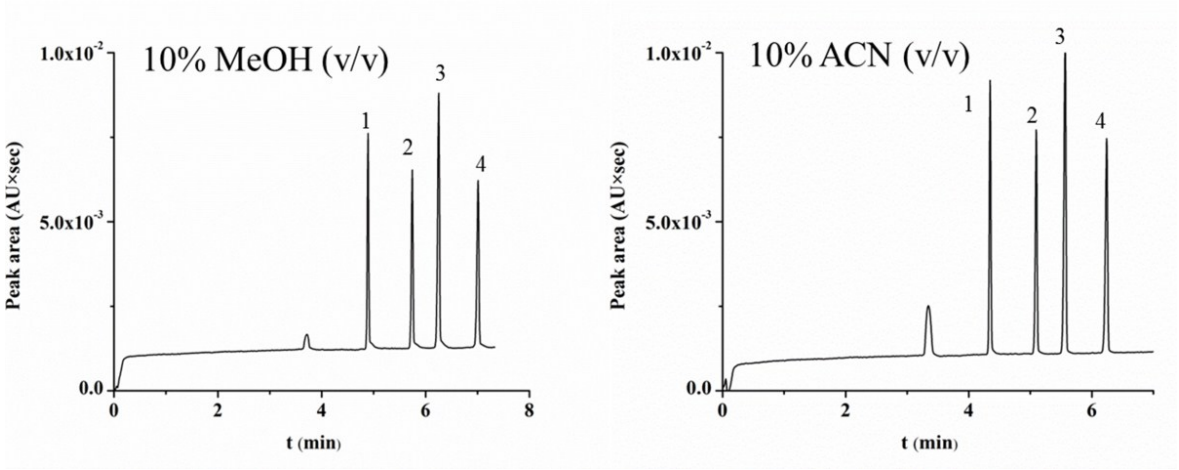

Fig. S5 Effect of ACN contents on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

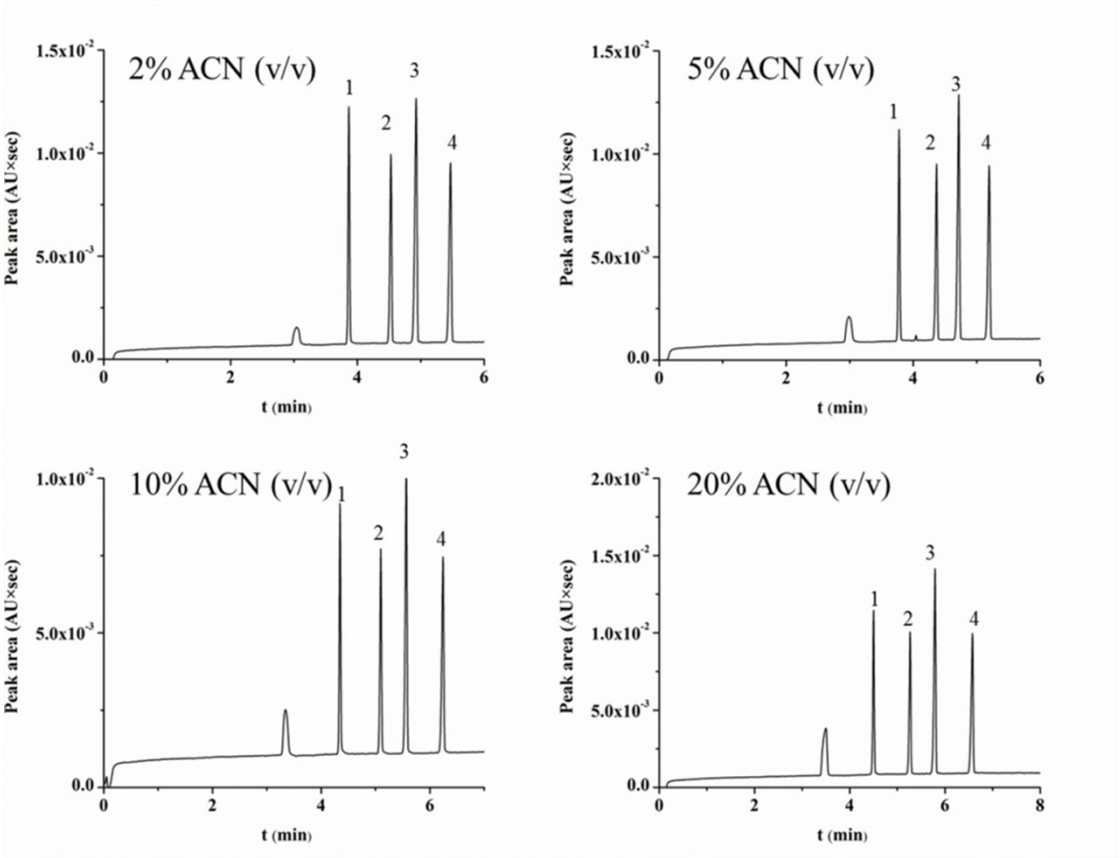

Fig. S6 Effect of separation voltage on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

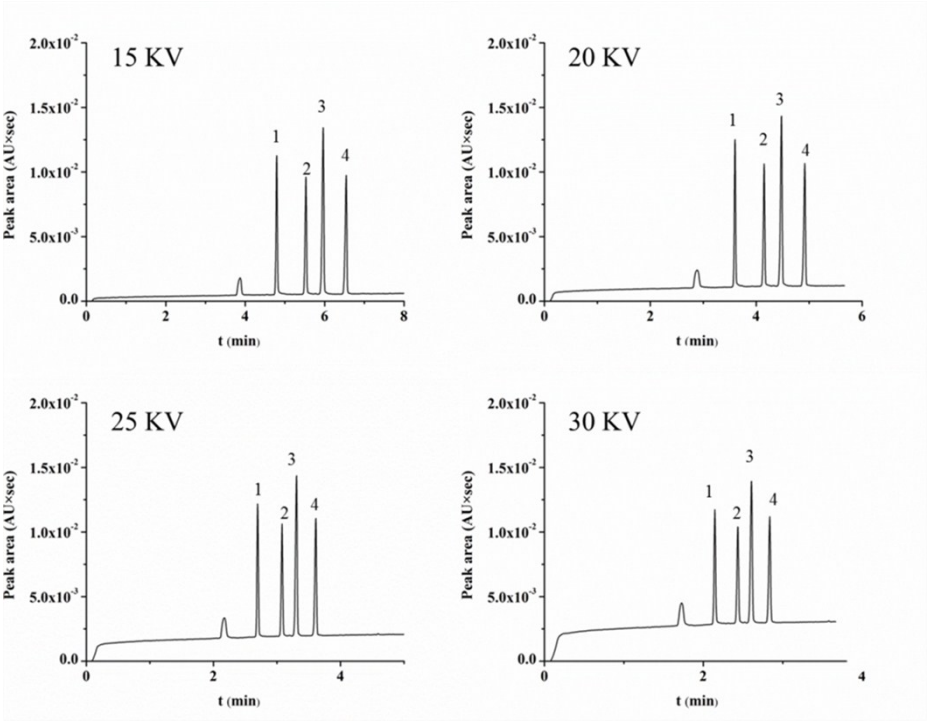

Fig. S7 Effects of (A) volume of extraction solvent and (B) volume of disperser solvent on the peak area of the four SAs. Extraction conditions: (A) sample volume, 5 mL; dispersive solvent, 800 μL DMSO and (B) sample volume, 5 mL; extraction solvent, 400 μL C_6H_5Cl. CE conditions: 20 mmol/L NaH_2PO_4 containing 10% (v/v) ACN at pH=7.8, injection 5 s with 0.5 psi, +20 kV applied voltage.

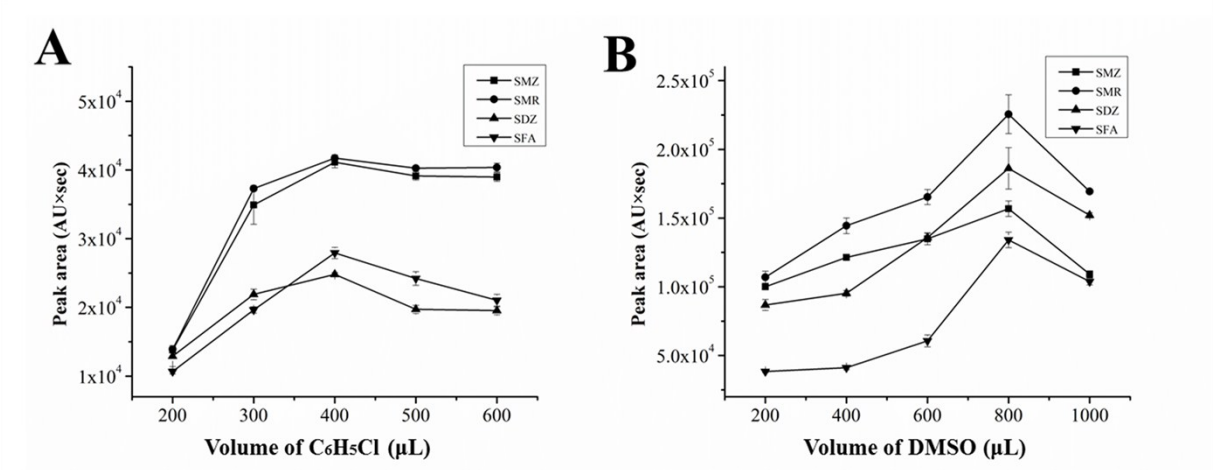

Fig. S8 Effect of NaCl contents on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

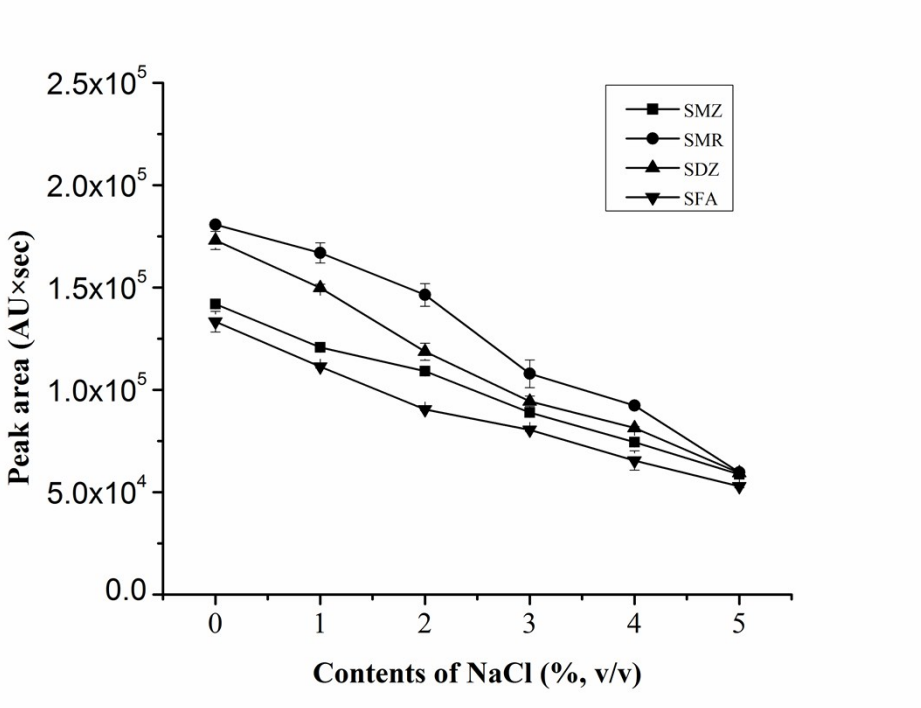

Fig. S9 Effect of type of the redissolved solvent on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

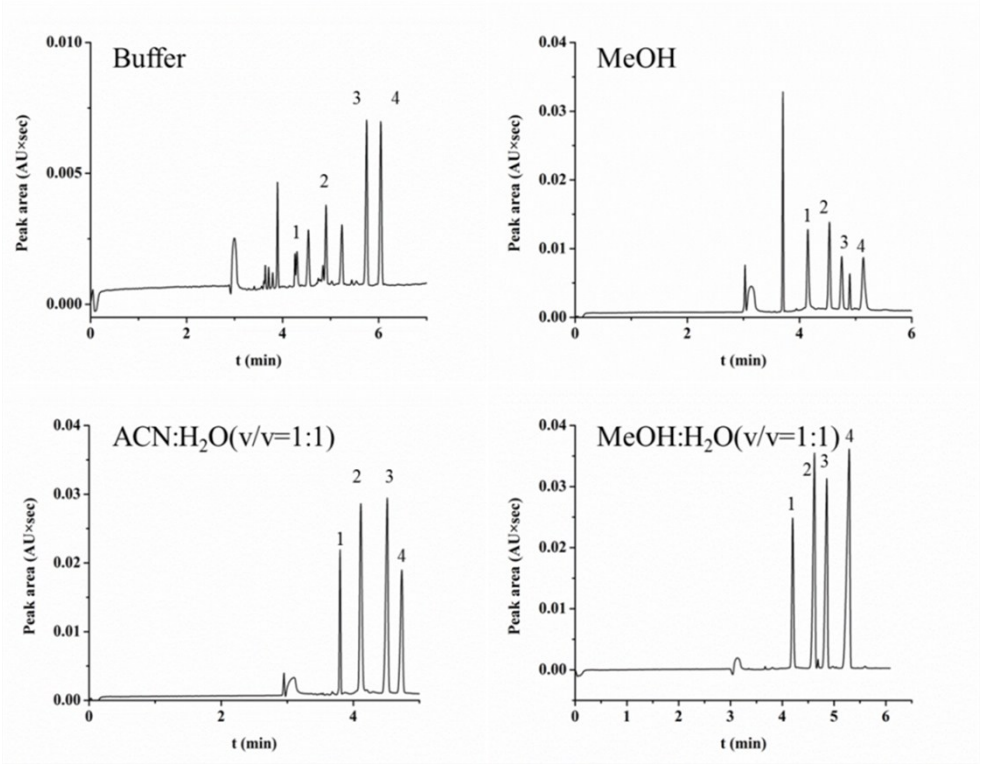

Fig. S10 Effect of volume of the redissolved solvent on the separation of the four SAs. Peak identification: (1) SMZ; (2) SMR; (3) SDZ; (4) SFA.

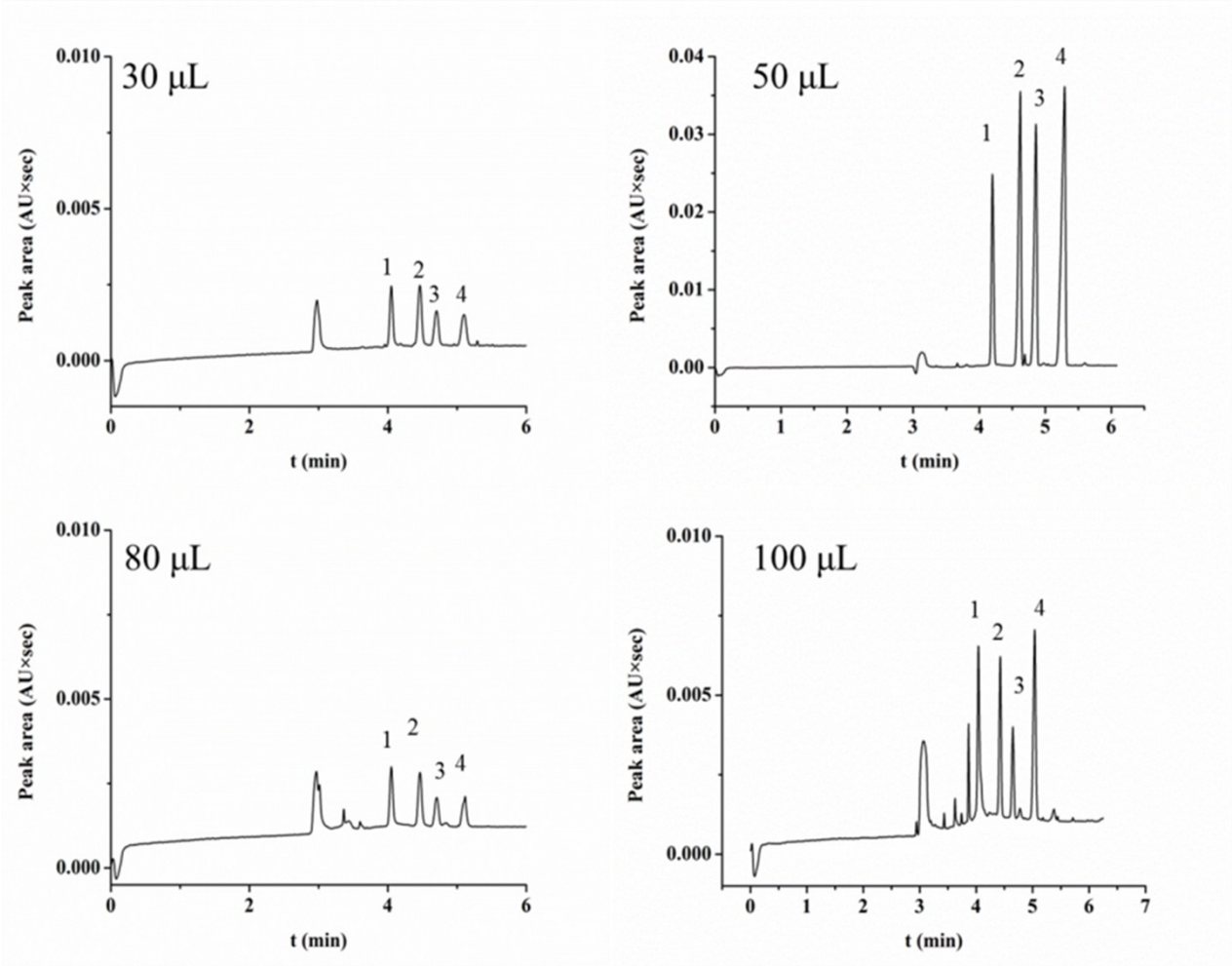

Fig. S11 Effects of (A) water injection time, (B) injection voltage, (C) injection time, and (D) assisted pressure on the peak area of the four SAs. Sample conditions: SA standard solution at 1.0×10^4 ng/mL individual. FASI conditions: the assisted pressure of electric injection is 0.5 psi (ca. 3.45 kpa), 3 s injection time of water plug, pressure injection at -10kV voltage, and injection time of 0.5 min.

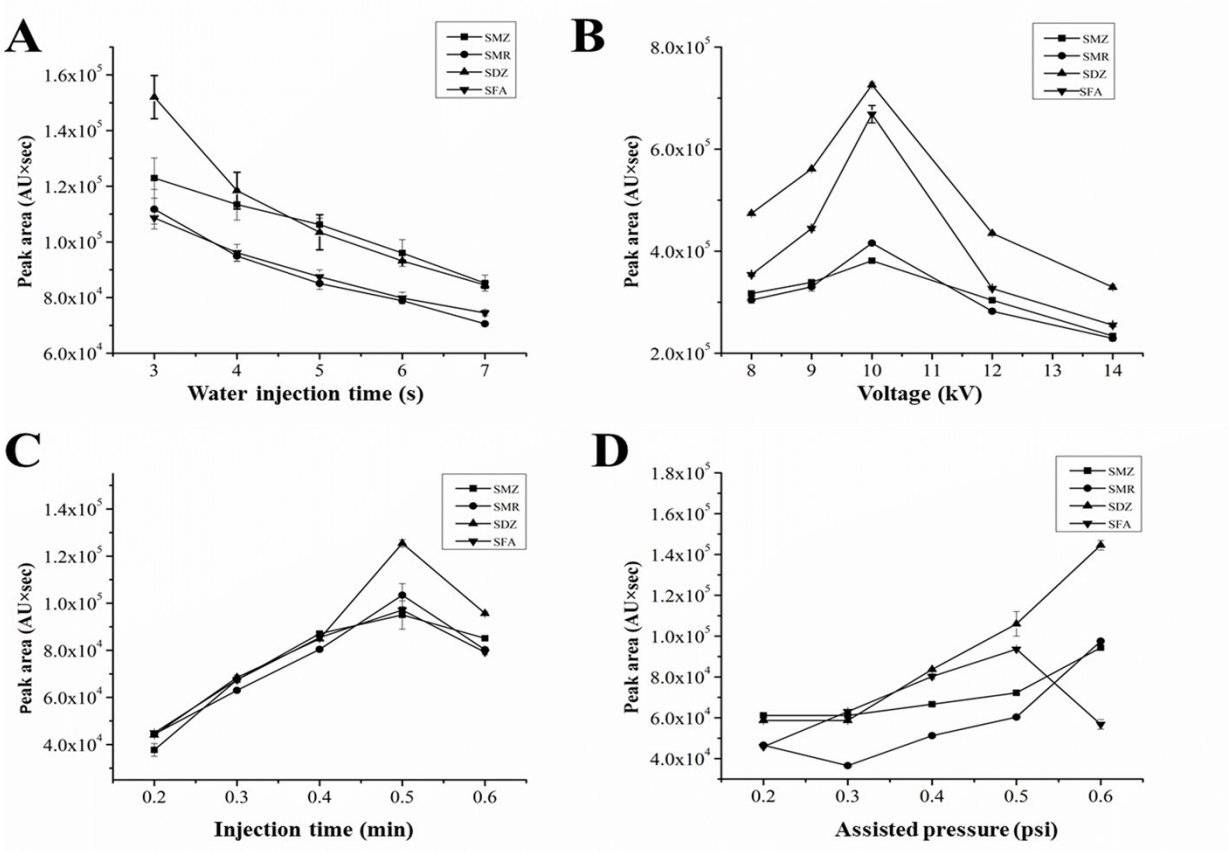

Table S1 Analytical performance of the DLLME-FASI-CE method for the determination of four SAs in standard solution.

	Calibration equation[a]		Correlation coefficient (r)	Linear range (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)	SEF	
	k (mean±SD)	b (mean±SD)					DLLME	DLLME-FASI
SMZ	7915.9±12.300	1153.80±837.0	0.9938	2.0–20.0	0.67	2.23	29.3	206
SMR	930.9±10.400	455.31±231.7	0.9904	1.0–20.0	0.34	0.94	31	166
SDZ	12734.0±7.804	367.00±198.2	0.9942	1.0–20.0	0.33	1.10	46.2	185
SFA	12028.0±5.100	5429.00±1250.0	0.9931	2.0–20.0	0.75	2.50	27	150

[a] $y = kx + b$; based on peak area.

Table S2 Method precision of migration time and peak area in standard solution.

SAs	RSD[a] (%, *n*=5)			
	Intra-day		Inter-day	
	Migration time	Peak area	Migration time	Peak area
SMZ	0.19	2.02	1.09	5.17
SMR	0.25	1.86	1.14	3.76
SDZ	0.29	2.16	1.74	3.97
SFA	0.32	2.82	1.05	4.34

[a] At individual concentrations of 1.0×10^4 ng/mL.

Table S3 Method precision of migration time and peak area in seawater sample.

SAs	RSD[a] (%, *n*=5)			
	Intra-day		Inter-day	
	Migration time	Peak area	Migration time	Peak area
SMZ	0.60	7.13	4.21	5.36
SMR	0.77	5.30	3.09	7.68
SDZ	0.80	6.79	3.99	10.47
SFA	0.47	2.04	3.72	11.15

[a] At individual concentrations of 1.0×10^4 ng/mL.

Table S4 Recoveries obtained for the determination of four SAs in spiked tap, lake and river water samples (*n*=5).

SAs	Spiked (ng/mL 10^3)	Tap water			Lake water			Seawater		
		Found±SD (10^3 ng/mL)	Recovery (%)	RSD (%)	Found±SD (10^3 ng/mL)	Recovery (%)	RSD (%)	Found±SD (10^3 ng/mL)	Recovery (%)	RSD (%)
SAs	0	ND[a]			ND[a]			ND[a]		
SMZ	0.1	0.093±0.004	93.0	4.30	0.097±0.005	97.0	5.15	0.105±0.003	105.0	2.85
	2.0	1.950±0.037	97.5	1.89	2.010±0.033	101.7	1.65	2.130±0.180	106.5	7.45
	10.0	10.120±0.310	101.2	3.06	10.230±0.270	102.0	2.64	9.930±0.400	99.0	4.06
SMR	0.1	0.095±0.003	95.0	3.15	0.097±0.002	97.0	2.06	0.102±0.003	102.0	2.94
	2.0	1.920±0.040	96.0	2.08	2.030±0.220	102.3	6.80	2.160±0.130	108.0	6.01
	10.0	10.120±0.310	87.7	3.56	9.930±0.135	99.3	1.36	10.130±0.370	101.3	3.74
SDZ	0.1	0.091±0.003	91.0	3.29	0.095±0.002	95.0	2.10	1.080±0.050	108.0	4.62
	2.0	1.930±0.090	96.5	4.67	1.980±0.170	102.0	5.58	2.160±0.154	108.0	7.12
	10.0	9.810±0.320	98.0	3.24	10.300±0.140	103.0	1.37	10.430±0.730	104.3	7.08
SFA	0.1	0.093±0.002	93.0	2.15	0.102±0.003	112.0	2.94	0.108±0.004	108.0	3.70
	2.0	1.950±0.060	97.5	3.07	2.070±0.160	103.5	6.72	2.010±0.022	100.5	1.09
	10.0	10.270±0.210	102.7	2.03	9.980±0.320	99.8	3.24	10.190±0.410	102.0	4.06

[a] Not detected.

Table S5 Analytical performance comparison of DLLME-FASI-CE with other reported methods for determination of SAs.

SAs	Pretreatment method	Detection technique	Migration time (min)	Linearity range	LODs	LOQs	EF/SEF	Sample	Ref.
Sulfadiazine, sulfathiazole, sulfamerazine , sulfamethazine, sulfamethoxypyridazine	MSPE	HPLC	~14	3.97−1000 (ng/g)	1.73−5.23 (ng/g)	3.97−15.89 (ng/g)	–	Meat sample	[1]
Sulfaguanidine,sulfadiazine, sulfathiazole,sulfamerazine, sulfamethizole,sulfamethazine,sulfamethoxypyridazine,sulfachloropyridazine,sulfamethoxazole, sulfadimethoxine, sulfasalazine	SPE	LC-MS	~25	50–500 (μg/kg)	25 (μg/kg)	–	–	Milk and chicken muscle	[4]
Sulfadiazine, sulfathiazole, sulfamethazine,Sulfapyridine sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole,sulfadimethoxine, sulfisoxazole, sulfaquinoxaline	microextraction	HPLC	~30	0.05–150(μg/L) ;0.5–150(μg/L)	0.008–0.0019 (μg/L); 0.077–0.350 (μg/L)	0.23–1.05 (μg/L);0.025–0.057 (μg/L)	–	Milk and water sample	[5]
Sulfadiazine,sulfathiazole, sulfamethazine,sulfamerazine, sulfanilamide, sulfamethoxypyridazine, sulfachloropyridazine, sulfacetamide, sulfamethoxazole, sulfadimethoxine	Salting-out-LLE	HPLC-fluorescence	~35	0–100 (ng/g)	1.5–2 (ng/g)	5–100 (ng/g)	–	Honey	[7]

Sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfameter, sulfamethizole, sulfamethazine, sulfamethoxypyridazine,sulfachloropyridazine, sulfamethoxazole, sulfamonomethoxine, sulfadimethoxine, sulfisoxazole, sulfadoxine	polymer monolith microextraction	LC/MS	~14	5–2000 (ng/g)	0.4–5.7 (ng/mL); 0.9–9.8 (ng/g)	1.8–19(ng/g) 2.9–32.8 (ng/g)	9.4–19.6	Milk and egg	[8]
Sulfadimethoxine, sulfadiazine, sulfapyridine, sulfamerazine, sulfamethazine, sulfamonomethoxine, sulfachloropyridazine sulfamethoxazole	MIP-SPE	HPLC	~14	25−5000 (μg/L)	0.2−3 (g/L)	–	–	Blood	[9]
Sulfadimethoxine, sulfadiazine, sulfapyridine,sulfamerazine, sulfamethazine, sulfamonomethoxine, sulfachloropyridazine,sulfamethoxazole	MSPE	UV	~15	1–100 (μg/L)	0.2–3 (μg/L)	–	–	Waters	[10]

Sulfathiazole,sulfamethoxazole, sulfamethizole,sulfadimethoxine, tetracycline,Hydrochloride,oxytetracyclinehydrochloride,sulfamethazine,chlortetracycline,tiamulin fumarate	SPE	LC-MS	~30	1–1000 (μg/L)	–	0.5–8 (μg/L)		Swine wastewater	[11]
Sulfonamides**,** sulfadinidin, sulfadoxin**,** sulfadiazine, sulfamerazin**,** sulfapyridine	DLLME	CE-UV	~5	0.5–50 (μg/L)	0.020–0.570 (μg/mL)	–	–	Water	[12]
Sulfaguanidine, sulfanilamide, sulfaomidine, sulfadiazine, sulfisthiazole, sulfapyridine, sulfamerazine, sulfamethazine, sulfamethizole, sulfameter, sulfamonomethoxine, sulfachloropyridazine, sulfadoxin, sulfamethoxazole, sulfisoxazole, sulfabenzamide, sulfadimethoxine, sulfaquinoxaline	SPE	Nano-LC/MS	~35	50–1800 (μg/kg)	2–40 (μg/kg)	8–96 (μg/kg)	–	Honey, milk	[33]
Sulfadiazine, sulfathiazole, sulfamethazine, Sulfapyridine sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfadimethoxine, sulfisoxazole, sulfaquinoxaline	Microextraction	HPLC	~30	0.05–150 (μg/L)	0.008 –0.350 (μg/L)	0.025–0.057 (μg/mL) 0.23–1.05 (μg/mL)	25–463	Lake water, Milk	[34]

Sulfachloropyridazine,sulfaquinoxaline,sulfadiazine,sulfamerazine, sulfamethoxazole, sulfapyridine, sulfathiazole,sulfamonomethoxine	MSPE	UHPLC-MS/MS	~9	5.0–1000.0 (ng/L)	0.49–1.59 (μg/L)	1.64–5.29 (ng/L)	–	Water	[35]
Sulfaguanidine, sulfanilamide, sulfacetamide, sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfamether, sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine and sulfadoxine	LLE-SPE	HPLC-fluorescence	~60	2−100 (ng/g)	1−2 (ng/g)	2−5 (ng/g)	–	Honey	[45]
Sulfamethazine, sulfamerazine free acid, sulfadizine, sulfacetamide	DLLME	CE	~6	0.01−10 (μg/mL)	0.0020−0.063 (μg/mL)	0.0067−0.201 (μg/mL)	150−206	Water	This work