

**Supplementary material**

**Fabrication of a functionalized magnetic covalent organic framework composite as an efficient  
adsorbent for sulfonamides extraction from food samples**

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### **1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs**

The magnetic Fe<sub>3</sub>O<sub>4</sub> NPs were synthesized based on our previous work [1]. In brief, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g) and NH<sub>4</sub>OAc (3.85 g) were firstly dispersed in ethylene glycol (70 mL). After mechanically stirring for 60 min at the room temperature, the mixture was transferred into a Teflon-lined stainless-steel autoclave. The reaction was carried out at 200 °C for 16 h. And then, the product was collected via a magnet and washed with ethanol and ultrapure water, successively. Finally, the obtained product was dried in a vacuum oven at 60 °C for 12 h.

### **2. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@TbBd microspheres**

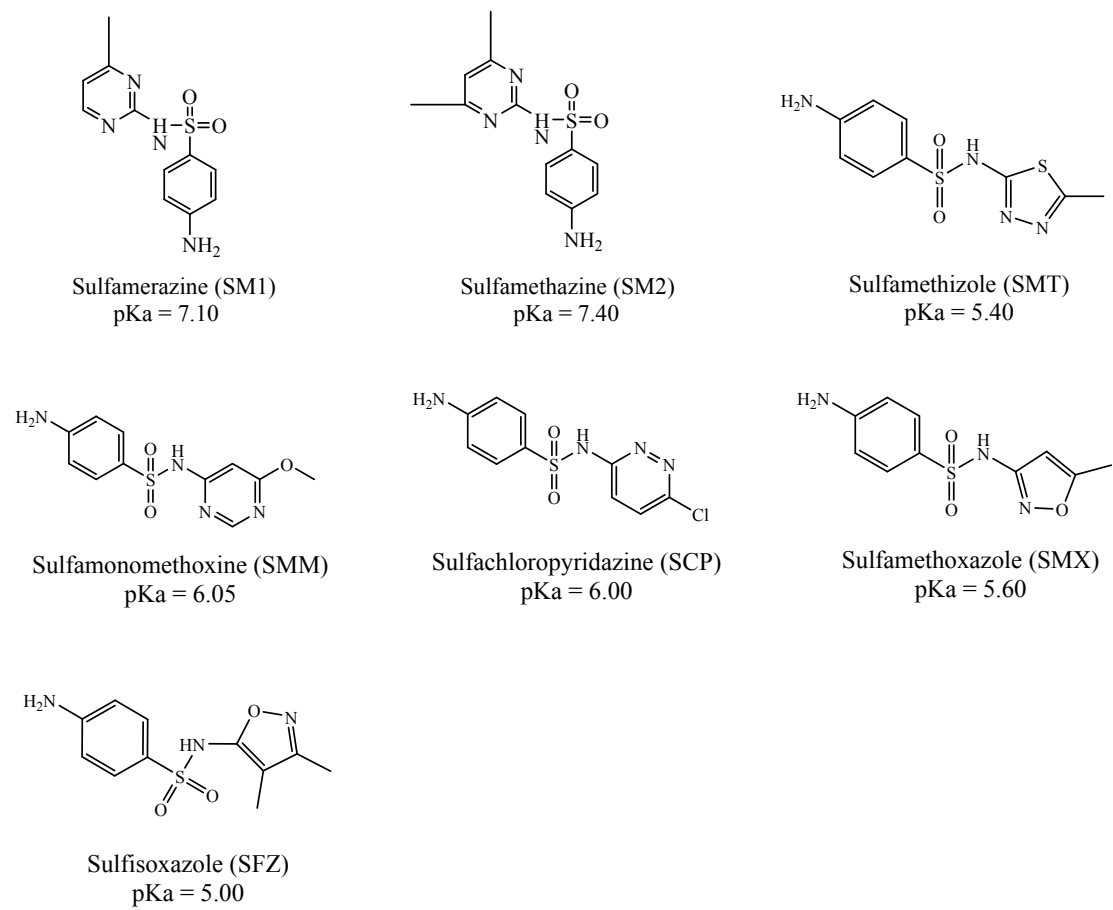
Typically, Fe<sub>3</sub>O<sub>4</sub> NPs (0.15 g) were added into DMSO (50 mL) with Tb (0.3 mmol) and Bd (0.45 mmol) [2]. Then, the mixture was ultrasonicated for 5 min. After that, anhydrous acetic acid (2 mL) was added slowly into the mixture. After incubation for 15 min at room temperature, the prepared Fe<sub>3</sub>O<sub>4</sub>@TbBd microspheres were collected by using a magnet and washed with tetrahydrofuran and anhydrous ethanol successively, then dried in vacuum at 50 °C for 8 h.

### **3. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH composites**

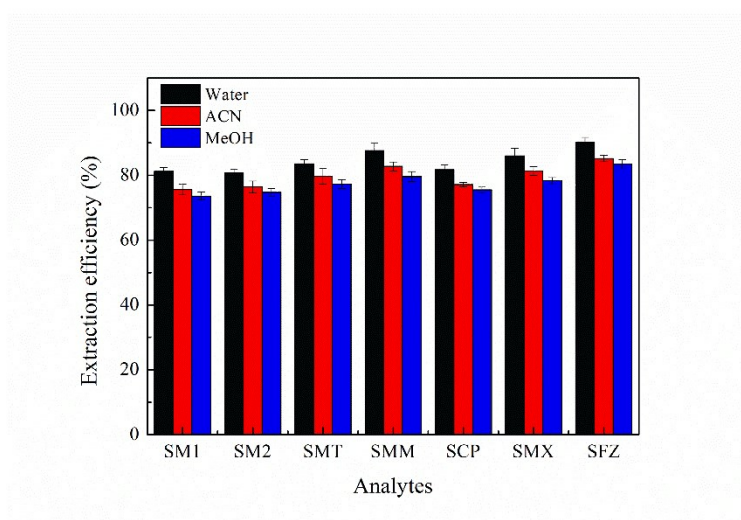
Firstly, the Fe<sub>3</sub>O<sub>4</sub>@COF-Au microspheres were synthesized [3]. In brief, Fe<sub>3</sub>O<sub>4</sub>@TbBd (0.06 g) was dissolved in MeOH (30 mL), 1% H<sub>2</sub>AuCl<sub>4</sub>·4H<sub>2</sub>O (320 μL) was added dropwise into the mixture, then the mixture was stirred for 4 h at 0 °C. Subsequently, 0.10 mol/L NaBH<sub>4</sub> methanol solution (1 mL) was added slowly stirring for another 3 h. The obtained precipitate was separated with a help of magnet, washed with methanol and dried under vacuum for 12 h at 60 °C. After that, the Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH microspheres were synthesized through MAA as the functionalized chemical to modify Fe<sub>3</sub>O<sub>4</sub>@TbBd-Au microspheres [4]. Fe<sub>3</sub>O<sub>4</sub>@TbBd-Au (0.05 g) was added to 0.29 mM MAA ethanol solution (10 mL) with stirring for 24 h at room temperature. The product was collected with magnet, washed by absolute

ethyl alcohol and distilled water, and dried under vacuum for 8 h at 50°C [5]. Finally, the

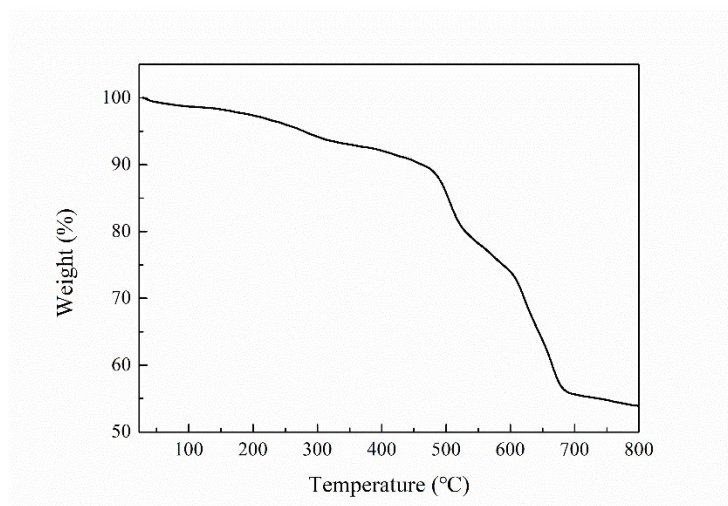
Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH composites were synthesized.



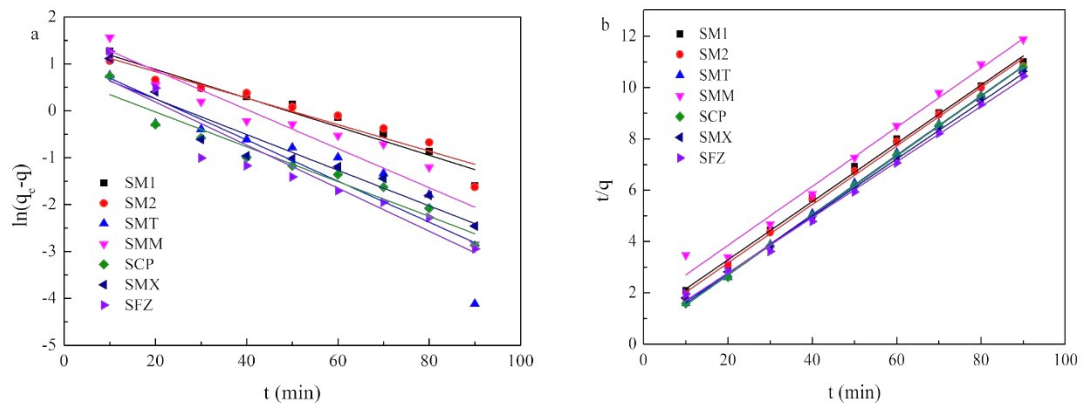
**Fig. S1** Chemical structures and pKa values of the target SAs.



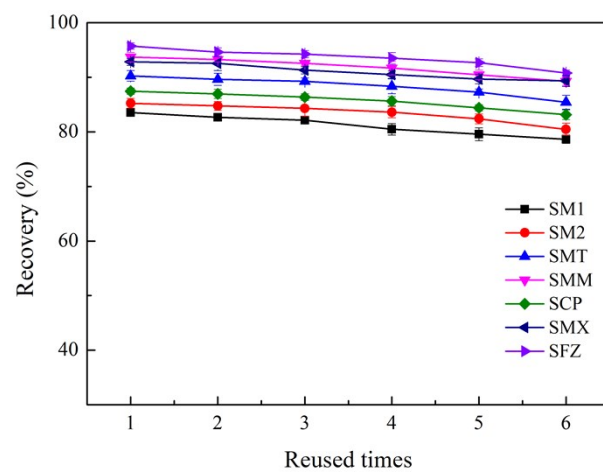
**Fig. S2** The comparison of the extraction efficiency in different solvents.



**Fig. S3** The TGA of the Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH.

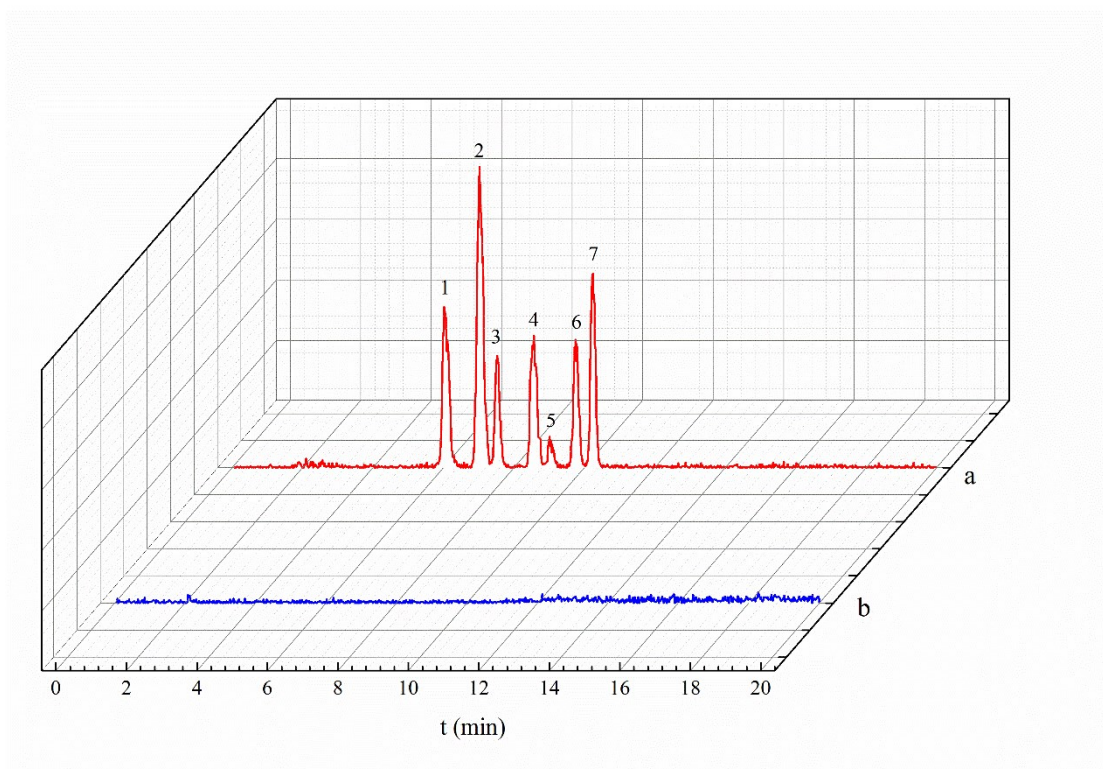


**Fig. S4** Adsorption kinetics of SAs on Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH. (a) two-parameter fit of  $\ln(q_e - q)$  with  $k_1$  using Eq. (2); (b) two-parameter fit of  $t/q$  with  $k_2$  using Eq. (3).

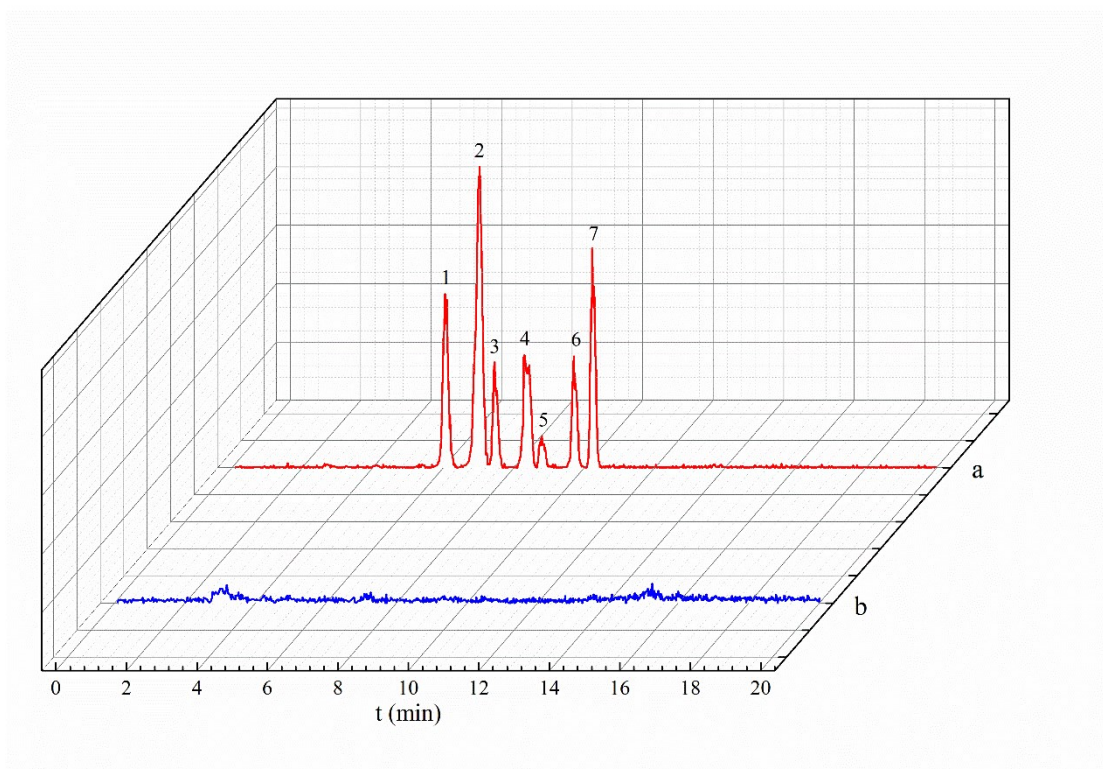


**Fig. S5** The reused times of the  $\text{Fe}_3\text{O}_4@\text{TbBd-COOH}$  towards seven SAs.





**Fig. S6** The typical chromatograms of (a) blank chicken sample spiked with 50  $\mu\text{g}/\text{kg}$  and (b) real chicken sample (Peak identification: 1, SM1; 2, SM2; 3, SMT; 4, SMM; 5, SCP; 6, SMX; 7, SFZ).



**Fig. S7** The typical chromatograms of (a) blank pork sample spiked with 50  $\mu\text{g}/\text{kg}$  and (b) real pork sample (Peak identification: 1, SM1; 2, SM2; 3, SMT; 4, SMM; 5, SCP; 6, SMX; 7, SFZ).

Table S1. Optimized HPLC-MS/MS conditions for the detection of SAs

Analyte	Precursor ions (m/z)	Product ions (m/z)	Declustering potential (V)	Collision energy (e V)	Retention time (min)
SM1	265.2	156.0* 172.2	43.1	21.4	5.82
SM2	279.1	124.0* 108.3	42.3	26.8	6.73
SMT	271.0	156.1* 215.3	26.0	27.5	7.14
SMM	281.1	156.2* 108.1	27.8	23.5	8.28
SCP	285.2	156.1* 107.8	100.4	39.5	8.64
SMX	254.2	156.0* 108.2	42.0	20.0	9.35
SFZ	268.1	156.2* 108.2	32.5	19.2	9.81

\* The product ion used for quantification.

Table S2. The kinetic parameters and coefficients of the pseudo-first order and pseudo-second order adsorption kinetic models for SAs onto Fe<sub>3</sub>O<sub>4</sub>@TbBd-COOH

Analyte	pseudo-first order			pseudo-second order		
	k <sub>1</sub>	q <sub>e</sub> (mg/g)	R <sup>2</sup>	k <sub>2</sub>	q <sub>e</sub> (mg/g)	R <sup>2</sup>
SM1	0.3056	4.465	0.9484	1.1165	8.997	0.9968
SM2	0.4593	3.009	0.9023	1.2576	8.983	0.9954
SMT	0.4389	3.113	0.7907	3.0107	8.681	0.9995
SMM	0.4165	5.439	0.8765	0.8651	8.670	0.9903
SCP	0.371	2.049	0.9439	3.5876	8.642	0.9998
SMX	0.380	2.756	0.9142	2.2459	9.004	0.9993
SFZ	0.4593	3.009	0.9023	2.0087	9.192	0.9981

Table S3. Calibration curve equations, correlation coefficients (R<sup>2</sup>), LODs and LOQs for SAs in a

chicken sample

Analyte	linear range (µg/kg)	linearity eq	R <sup>2</sup>	RSD (intra- day %)	RSD (inter- day %)	LODs (µg/kg)	LOQs (µg/kg)
SM1	0.5-100	y = 385x + 157	0.9987	2.8	4.2	0.1	0.3
SM2	0.5-100	y = 703x + 286	0.9995	4.3	5.3	0.2	0.7
SMT	1-100	y = 289x + 369	0.9998	5.3	6.5	0.4	1.3
SMM	1-100	y = 314x + 493	0.9997	3.6	4.8	0.4	1.3
SCP	1-100	y = 76x + 66	0.9994	4.2	5.1	0.3	1.0
SMX	0.5-100	y = 316x + 648	0.9993	3.9	5.6	0.3	1.0
SFZ	0.5-100	y = 506x + 429	0.9996	4.4	6.2	0.1	0.3

Table S4. Calibration curve equations, correlation coefficients ( $R^2$ ), LODs and LOQs for SAs in a pork

sample							
Analyte	linear range ( $\mu\text{g}/\text{kg}$ )	linearity eq	$R^2$	RSD (intra- day %)	RSD (inter- day %)	LODs ( $\mu\text{g}/\text{kg}$ )	LOQs ( $\mu\text{g}/\text{kg}$ )
SM1	0.5-100	$y = 270x + 249$	0.9998	3.6	5.3	0.1	0.3
SM2	0.5-100	$y = 525x + 289$	0.9999	4.2	5.7	0.1	0.3
SMT	0.5-100	$y = 156x + 396$	0.9997	2.8	4.6	0.2	0.7
SMM	0.5-100	$y = 185x + 405$	0.9998	5.2	6.8	0.3	1.0
SCP	1-100	$y = 49x + 126$	0.9996	5.1	6.4	0.4	1.2
SMX	0.5-100	$y = 170x + 538$	0.9999	3.8	5.3	0.2	0.7
SFZ	0.5-100	$y = 326x + 324$	0.9995	4.7	5.9	0.1	0.3

Table S5. Recovery and precision values of SAs from different spiked levels by the proposed method in beef samples

Analytes	Sample 1					Sample 2					Sample 3				
	ME	Recovery %			RSD %	ME	Recovery %			RSD %	ME	Recovery %			RSD %
		Low	Middle	High			Low	Middle	High			Low	Middle	High	
SM1	0.97	85.34	86.11	86.68	4.6	0.95	86.26	85.69	86.44	4.1	0.98	85.67	86.34	85.82	4.2
SM2	0.92	88.69	89.53	90.19	4.9	0.97	89.03	89.79	88.58	4.5	1.02	88.28	88.95	89.43	4.5
SMT	1.03	93.52	92.84	92.43	5.4	1.04	92.85	91.64	92.28	4.8	1.05	93.39	93.82	92.65	4.2
SMM	0.95	97.61	99.27	97.69	6.9	1.02	98.11	99.42	97.23	5.5	0.97	97.94	98.65	98.72	5.9
SCP	0.98	89.71	88.64	89.95	5.7	0.96	89.18	89.78	90.34	4.2	0.98	90.64	90.23	89.75	4.3
SMX	1.04	96.02	97.58	98.66	4.3	0.98	95.64	96.26	96.87	4.6	1.03	96.36	97.24	96.68	4.8
SFZ	1.05	100.22	99.63	101.74	5.2	1.03	101.47	102.61	101.82	4.5	1.02	99.78	100.64	99.23	5.7

Table S6. Recovery and precision values of SAs from different spiked levels by the proposed method in chicken samples

Analytes	Sample 1					Sample 2					Sample 3				
	ME	Recovery %			RSD %	ME	Recovery %			RSD %	ME	Recovery %			RSD %
		Low	Middle	High			Low	Middle	High			Low	Middle	High	
SM1	0.95	86.68	86.29	85.77	5.1	0.97	86.28	85.96	85.47	5.6	0.96	86.23	85.75	85.56	5.2
SM2	0.98	90.12	91.35	90.64	4.6	0.93	89.68	90.32	91.51	6.7	0.95	91.47	90.58	90.29	5.3
SMT	0.96	94.31	94.58	93.85	4.3	0.95	93.56	94.49	94.82	5.4	1.02	92.86	93.45	94.68	6.2
SMM	1.01	96.74	97.24	97.62	5.5	0.96	97.25	96.81	96.54	5.1	1.04	96.52	95.86	96.77	5.6
SCP	0.97	91.82	93.29	91.57	5.9	1.03	90.37	91.26	92.43	5.8	0.97	92.34	91.08	91.59	5.1
SMX	0.94	95.65	96.82	97.25	6.4	1.02	96.52	96.89	97.24	4.7	0.94	95.86	96.31	97.42	6.3
SFZ	1.03	99.85	101.34	99.36	5.3	0.96	98.76	99.21	100.53	6.5	0.98	99.27	99.83	101.64	5.4



Table S7. Recovery and precision values of SAs from different spiked levels by the proposed method in pork samples

Analytes	Sample 1					Sample 2					Sample 3				
	ME	Recovery %			RSD %	ME	Recovery %			RSD %	ME	Recovery %			RSD %
		Low	Middle	High			Low	Middle	High			Low	Middle	High	
SM1	0.96	86.94	85.63	85.78	6.1	0.95	85.62	86.36	85.67	5.3	0.98	85.86	86.52	87.77	5.2
SM2	1.03	90.39	91.42	90.65	5.6	0.98	91.23	90.66	90.48	4.8	0.93	90.82	90.49	92.11	5.4
SMT	1.02	93.76	94.38	94.51	5.3	1.03	94.52	94.83	93.56	5.1	0.95	94.28	94.83	93.42	4.9
SMM	0.95	96.85	96.57	97.36	4.8	0.97	96.82	97.37	98.56	5.7	0.96	96.57	95.88	97.24	5.5
SCP	0.97	90.56	91.23	91.87	5.4	0.98	91.28	91.76	92.15	4.9	1.02	91.68	92.43	91.89	5.2
SMX	0.94	94.87	96.34	96.57	5.5	0.96	95.86	96.48	95.39	5.2	1.05	95.39	96.48	94.82	5.6
SFZ	0.92	98.82	99.64	99.39	5.3	1.03	101.34	100.46	99.53	5.4	0.97	98.64	101.34	99.64	6.1

## References

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