## **Supporting Information**

Simultaneously quantitative detection of multiple hormones based on PS-MS: affinity capture by single antibody

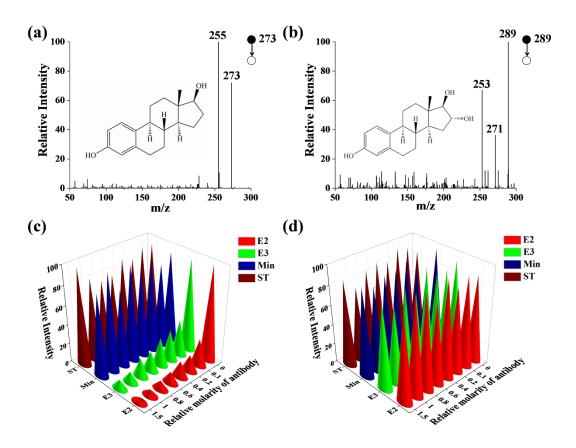
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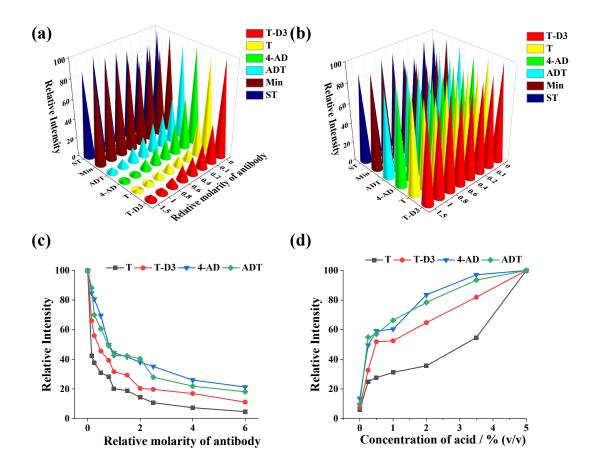
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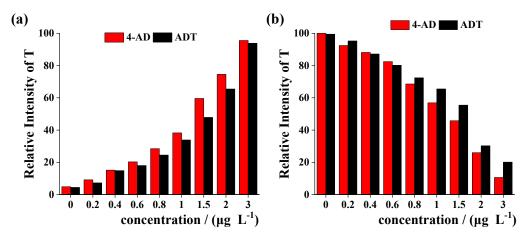
<sup>\*</sup>Prof. Sichun Zhang, Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China.



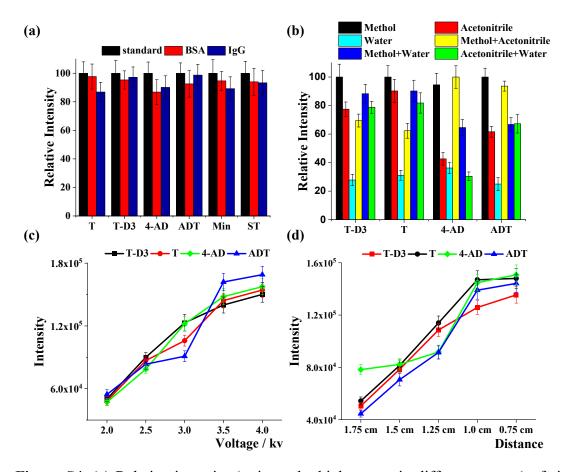
**Figure S1.** (a)-(b) MS/MS spectra of two hormones in standard samples: (a) estradiol (E2), (b) estriol (E3); (c)-(d) relative intensity (ratio to the highest one in different groups) of different hormones: (a)  $1.0 \mu g L^{-1}$  each hormone mixed with different molar concentration of E2 antibody, (b) paralleled samples to (a) just added with 5% (v/v) formic acid.



**Figure S2.** (a)-(b) Relative intensity (ratio to the highest one in different groups) of different hormones: (a) 1.0 μg L<sup>-1</sup> each hormones respectively mixed with different molar concentration of T antibody from another company, (b) paralleled samples to (a) just added with 5% (v/v) formic acid, (c) relative intensity (ratio to the highest one in different groups) of four mixed hormones (1.0 μg L<sup>-1</sup> for each) with different molar concentration of T antibody, (d) relative intensity (ratio to the highest one in different groups) of four mixed hormones (1.0 μg L<sup>-1</sup> for each) with 2.0 ×10<sup>-8</sup> mol L<sup>-1</sup> T antibody



**Figure S3.** Relative intensity of T (a) dissociative section; (b) captured section. (1  $\mu$ g L<sup>-1</sup> T, 5.0 ×10<sup>-8</sup> mol L<sup>-1</sup> T antibody mixed with different concentration of 4-AD or ADT respectively)



**Figure S4.** (a) Relative intensity (ratio to the highest one in different groups) of six hormones (1.0  $\mu$ g L<sup>-1</sup> for each) respectively mixed with 2.0 ×10<sup>-8</sup> mol L<sup>-1</sup> BSA and IgG compared with standard samples, (b)-(d) optimization results of PS-MS (the concentration of samples was all kept to 1  $\mu$ g L<sup>-1</sup>): (a) spray solvent, (c) ionization voltage, (d) the distance between paper and MS inlet.

**Table S1.** Calculated results of recovery in spiked serum to direct paper spray.

compound	Paper spray	Affinity process	Recovery/%
	$(\mu g/L)$	$(\mu g/L)$	
Testosterone	$0.04 \pm 0.005$	$0.04 \pm 0.004$	90.9
	$0.16\pm0.007$	$0.16\pm0.008$	98.8
	$0.61\pm0.022$	$0.58 \pm 0.033$	95.1
	$1.49\pm0.060$	$1.54 \pm 0.078$	103.4
Androsterone	$0.04\pm0.004$	$0.04\pm0.003$	107.5
	$0.16\pm0.010$	$0.15\pm0.010$	93.8
	$0.58 \pm 0.028$	$0.61\pm0.025$	105.2
	$1.47\pm0.069$	$1.45\pm0.087$	98.6
Androstenedion	$0.04\pm0.005$	$0.04\pm0.004$	95.2
e			
	$0.16\pm0.008$	$0.15 \pm 0.009$	96.8
	$0.64 \pm 0.024$	$0.62\pm0.030$	96.9
	$1.50\pm0.071$	$1.55\pm0.090$	103.3