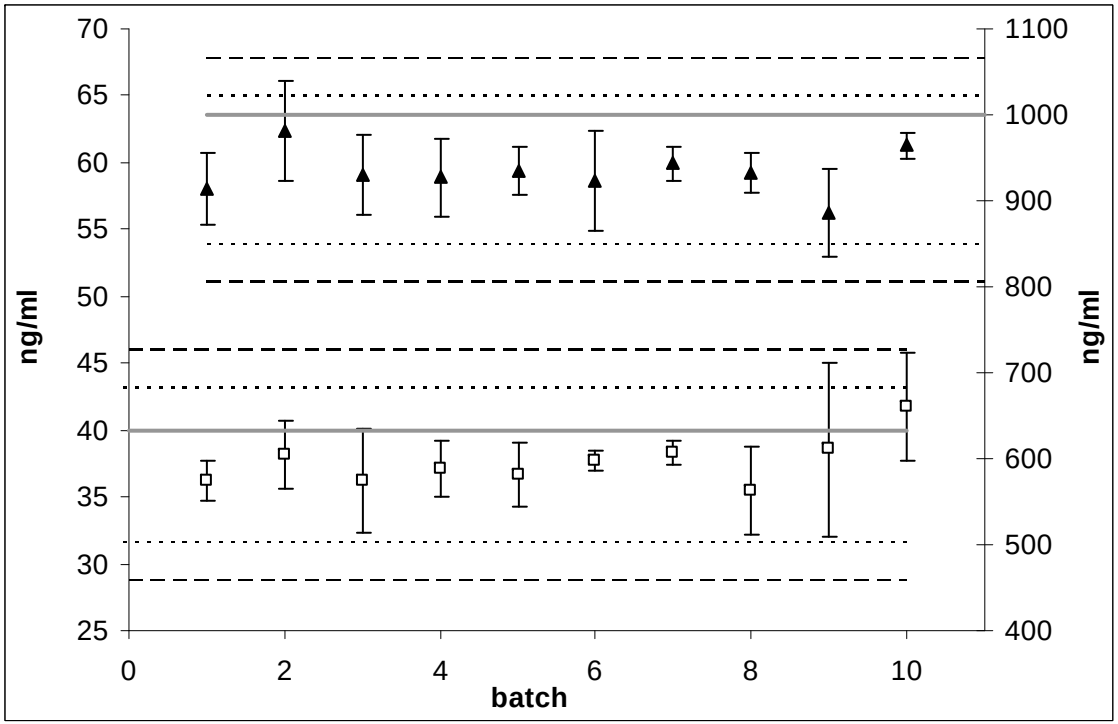
Supplemental fig 1)



Supplemental fig 1)
Inter and intra variation plot of the quality control samples low (QCL) and high (QCH) for testosterone glucuronide (TG). The open squares corresponds to QCL (y-scale at the left) and the filled triangles corresponds to QCH (y-scale at the right), with vertical bars showing the inter variation. The dotted lines correspond to ± 2 and 3 SD, respectively. The bold gray lines are the theoretical concentrations of TG.

Supplemental Table 1)

Ion transitions and collision offset used to detect the following target analytes:
testosterone glucuronide (TG and TG-d_3), testosterone sulfate (TS and TS-d_3), epitestosterone glucuronide (EPG and EPG-d_3), epitestosterone sulfate (EPS and EPS-d_3), dihydrotestosterone glucuronide (DHTG and DHTG-d_3) dihydrotestosterone sulfate (DHTS and DHTS-d_3), androsterone glucuronide (AG and AG-d_4), androsterone sulfate (AS and AS-d_4), etiocholanolone glucuronide (ETG) , etiocholanolone sulfate (ETS and ETS-d_5)

target analyte	Precursor	Precursor ion	Product ion	Collision offset voltage (V)
TG	$[M+H]^+$	466	97	29
TG-d_3	$[M+H]^+$	469	292	19
TS	$[M-H]^-$	367	97	33
TS-d_3	$[M-H]^-$	370	98	37
EPG	$[M+H]^+$	466	289	11
EPG-d_3	$[M+H]^+$	469	292	11
EPS	$[M+H]^+$	369	97	28
EPS-d_3	$[M+H]^+$	372	97	25
DHTG	$[M+NH_4]^+$	485	273	13
DHTG-d_3	$[M+NH_4]^+$	488	276	13
DHTS	$[M-H]^-$	369	97	41
DHTS-d_3	$[M-H]^-$	372	98	41
AG	$[M+NH_4]^+$	485	273	17
AG-d_4	$[M+NH_4]^+$	489	277	13
AS	$[M-H]^-$	369	97	41
AS-d_4	$[M-H]^-$	373	98	39
ETG	$[M+NH_4]^+$	485	273	17
ETS	$[M-H]^-$	369	97	41
ETS-d_5	$[M-H]^-$	374	98	39

Supplemental table 2)
Statistical summary of the quality control samples

target analyte	QCL			QCH		
	Conc (ng/ml)	*RSD (%)*	*Bias (%)*	*Conc (ng/ml)*	*RSD (%)*	*Bias (%)*
TG	40	7,71	-6.61	1000	4,65	-6.50
EPG	40	9,22	8.69	1000	4,87	12.00
DHTG	20	9,06	4.97	500	6,27	9.90
ETG	108	13,0	59.6 3.42*	2700	13,0	-5.88
AG	200	11,4	63.2 3.19*	5000	11,18	-4.32
TS	20	9,73	-10.23	500	4,17	-7.07
EPS	20	16,6	-8.28	500	12,3	-11.7
DHTS	20	7,43	-1.70	500	4,47	-2.31
ETS	80	5,16	40.8 15.8*	2000	6,21	-2.25
AS	80	9,54	13.8	2000	6,24	-9.05

*=Bias after adjustment for the content of steroid conjugate in the urine blank samples used for the control sample.