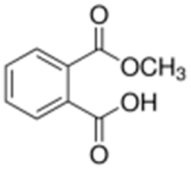
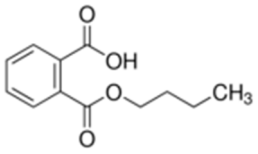
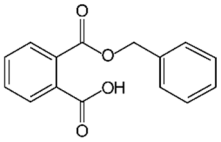
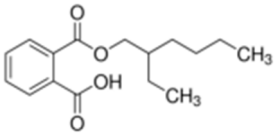
Supplementary Materials

Table S1. Physicochemical properties of the analytes selected for this study.

Analyte	Chemical Structure	pKa	Log P
Monomethyl phthalate (MMP)		3.08	1.13
Monobutyl phthalate (MBP)		3.08	2.96
Monobenzyl phthalate (MBzP)		3.08	3.36
Mono-(2-etylhexyl) phthalate (MEHP)		3.08	4.66

*Data obtained from data base Chemcalize, Pubchem and HMDB.

Table S2. Experiments of the simplex lattice design performed to evaluate desorption solvent.

Exp.	Ultrapure water pH 8 (%)	MeOH (%)	ACN (%)
1	100	0	0
2	0	50	50
3	0	100	0
4	0	0	100
5 (C)	33,3	33,3	33,3
6	50	50	0
7 (C)	33,3	33,3	33,3
8	50	0	50
9 (C)	33,3	33,3	33,3

Table S3. Experiments performed for the evaluation of desorption step with a Doehlert design.

Exp.	Desorption cycles	ACN volume (µL)
1	1	225
2	3	150
3 (C)	5	225
4	7	150
5	9	225
6 (C)	5	225
7	7	300
8	3	300
9 (C)	5	225

Table S4. Experiments performed for the evaluation of the extraction step with a Doehlert design.

Exp.	Extraction cycles	Extraction cycle volume (µL)
1	3	500
2	4	300
3 (C)	5	500
4	6	700
5	7	500
6 (C)	5	500
7	6	300
8	4	700
9 (C)	5	500

Table S5. Experiments performed in the Youden method.

Exp.	Urine volume (µL)	Sample pH	Extraction cycle volume (µL)	Extraction cycle	Washing cycles	ACN Volume (µL)	Desorption cycles
1	490	2.0	700	7	2	225	1
2	490	2.0	720	7	3	250	2
3	490	2.2	700	8	2	250	2
4	490	2.2	720	8	3	225	1
5	510	2.0	700	8	3	225	2
6	510	2.0	720	8	2	250	1
7	510	2.2	700	7	3	250	1
8	510	2.2	720	7	2	225	2

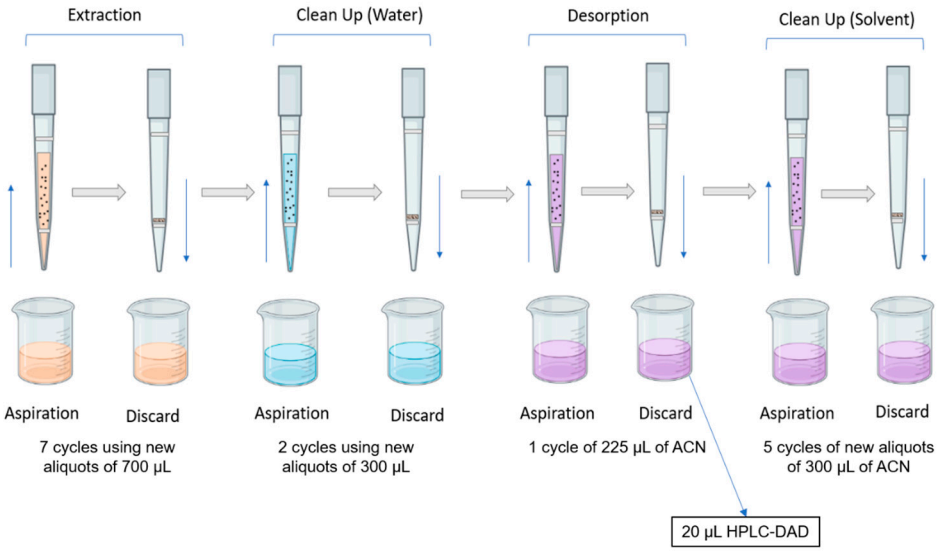


Figure S1. A figure of the steps performed for the DPX procedure.

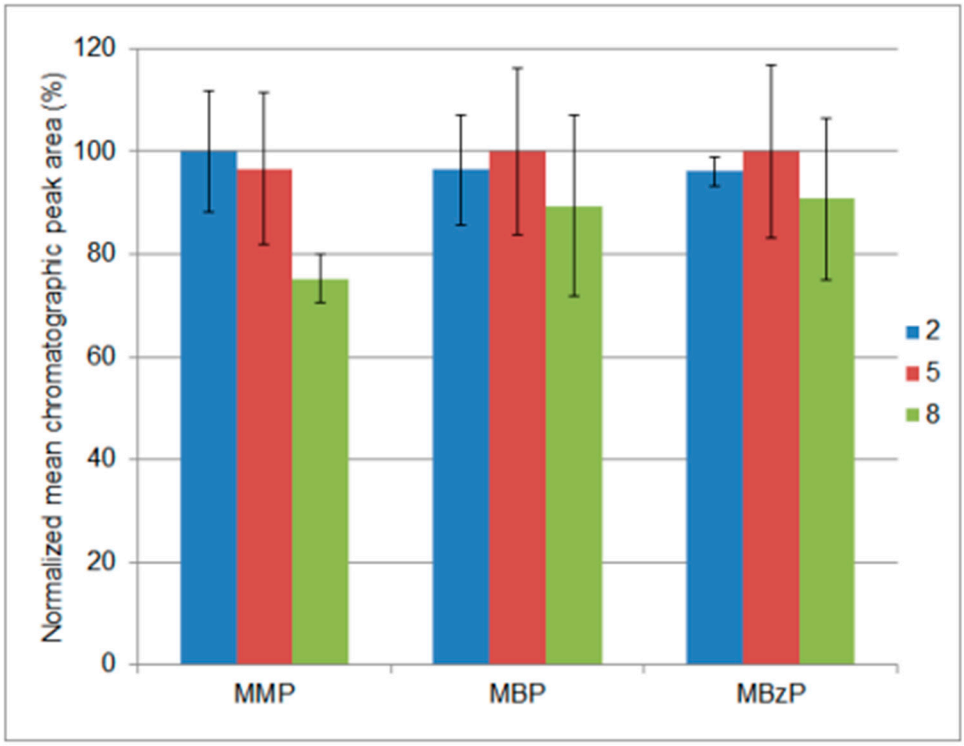


Figure S2. Bar graph obtained for the optimization of the washing cycles (2, 5 and 8). (Experimental conditions: 3.5 mL of urine adjusted to pH 3.0 and spiked at 300 μg L^{-1}. Extraction was performed with 5 cycles of 700 μL of sample using new aliquots, using variable washing cycles of 300 μL of ultrapure water and desorption using 5 cycles of 200 μL of ACN:MeOH (50:50, v:v)).

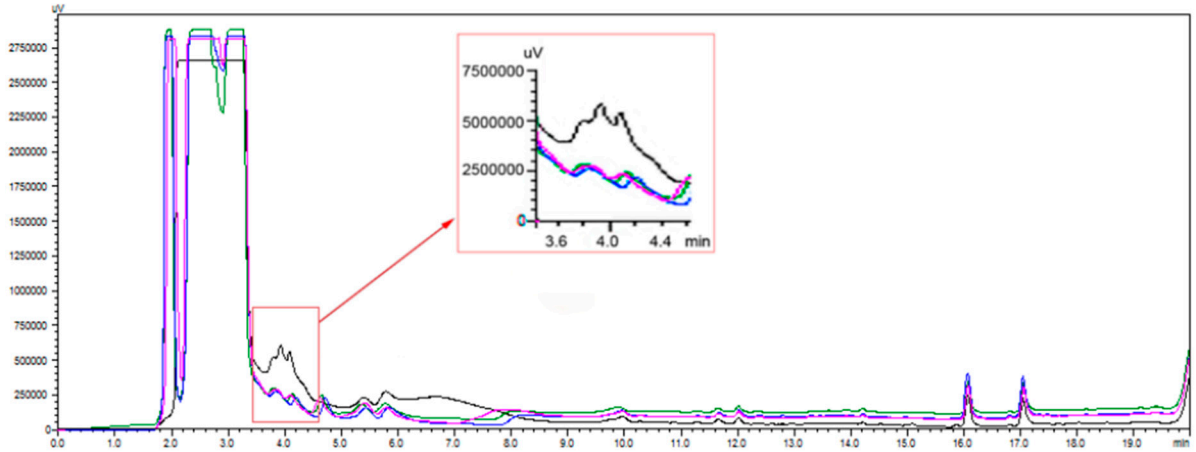


Figure S3. Comparative Chromatogram with detection wavelength of 210 nm using different washing cycles of ultrapure water between extraction and desorption, 2 cycles (pink), 5 cycles (blue) and 8 (green) and none (black).

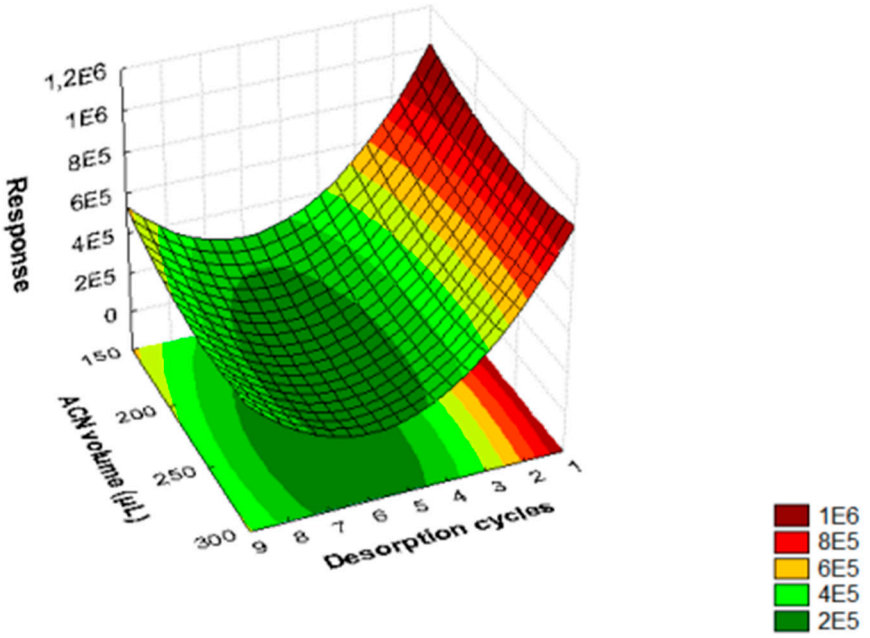


Figure S4. Response surface obtained for the Doehlert design used to evaluate desorption cycles and ACN volume. (Conditions: 3.5 mL of urine adjusted at pH 3.0 and spiked at 300 µg L^{-1}. Extraction was performed with 5 cycles of 700 µL of sample using new aliquots, followed by 2 cycles of 300 µL of ultrapure water and desorption using variable number of cycles and ACN volume).

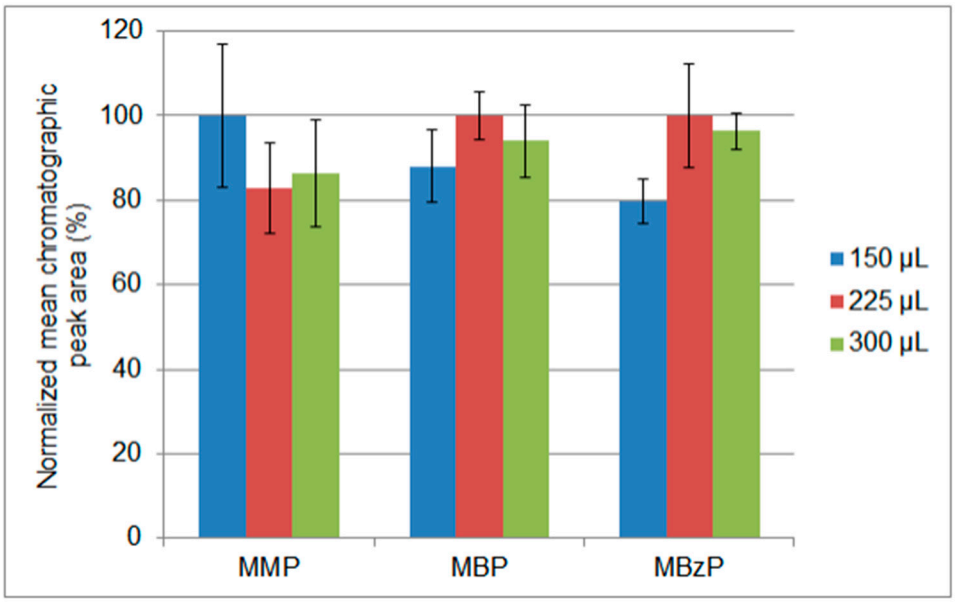


Figure S5. Bar graph obtained for the evaluation of ACN volume. (Conditions: 3.5 mL of urine adjusted at pH 3.0 and spiked at 300 µg L^{-1}. Extraction was performed with 5 cycles of 700 µL of sample using new aliquots, followed by 2 cycles of 300 µL of ultrapure water and desorption using 1 cycle of different volumes of ACN).

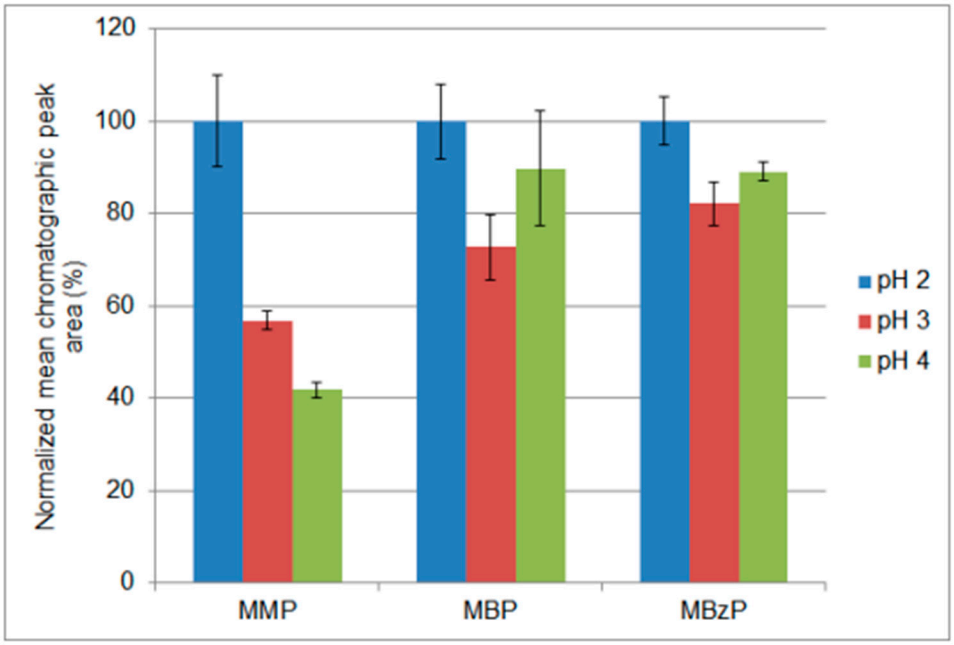


Figure S6. Bar graph obtained for the optimization of sample pH. (Experimental conditions: 4.9 mL of urine sample adjusted at variable pH and spiked at 300 μg L^{-1}. Extraction was performed with 7 cycles of 700 μL of sample for each cycle using new aliquots, followed by 2 cycles of 300 μL of ultrapure water and desorption using 1 cycle of 225 μL of ACN).

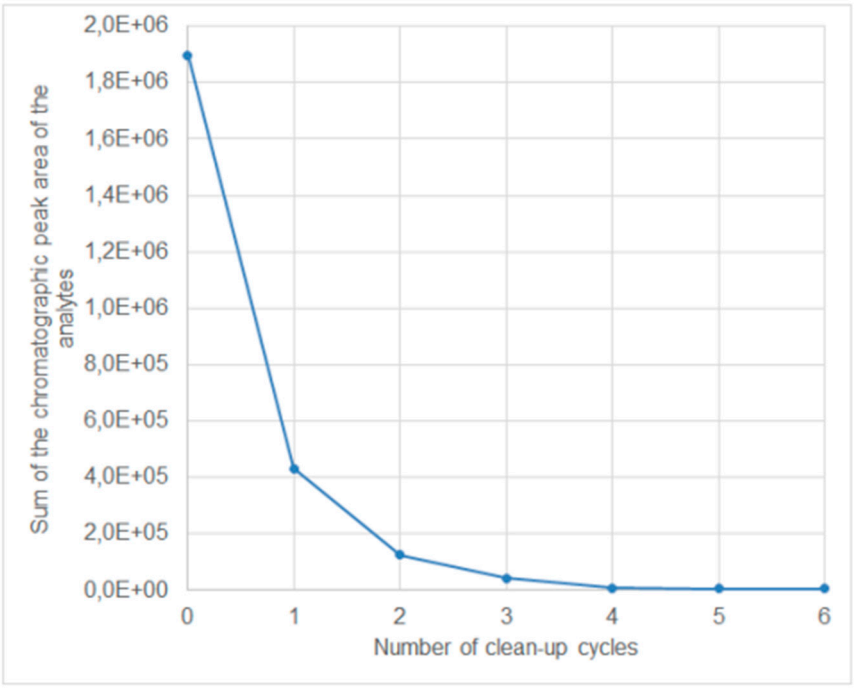


Figure S7. Graph obtained for the study of the clean-up step. (Experimental conditions: 4.9 mL of urine sample adjusted at pH 2.0 and spiked at 300 μg L^{-1}. Extraction was performed with 7 cycles of 700 μL of sample for each cycle using new aliquots, followed by 2 cycles of 300 μL of ultrapure water and desorption using 1 cycle of 225 μL of ACN).

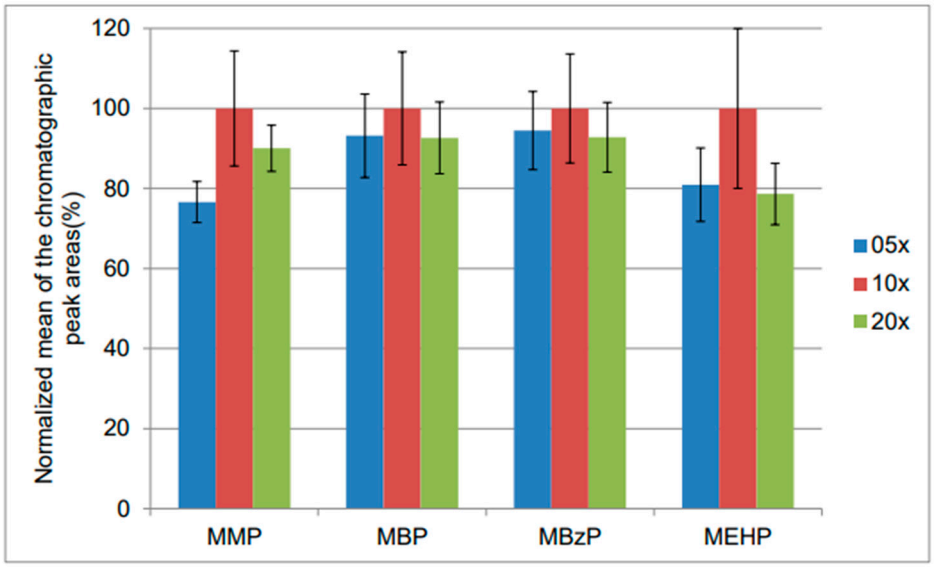


Figure S8. Bar graph obtained for urine dilution evaluation. (Experimental conditions: 4.9 mL of diluted urine sample adjusted at pH 2.0 and spiked at 300 μg L^{-1}. Extraction was performed with 7 cycles of 700 μL of sample for each cycle using new aliquots, followed by 2 cycles of 300 μL of ultrapure water and desorption using 1 cycle of 225 μL of ACN).

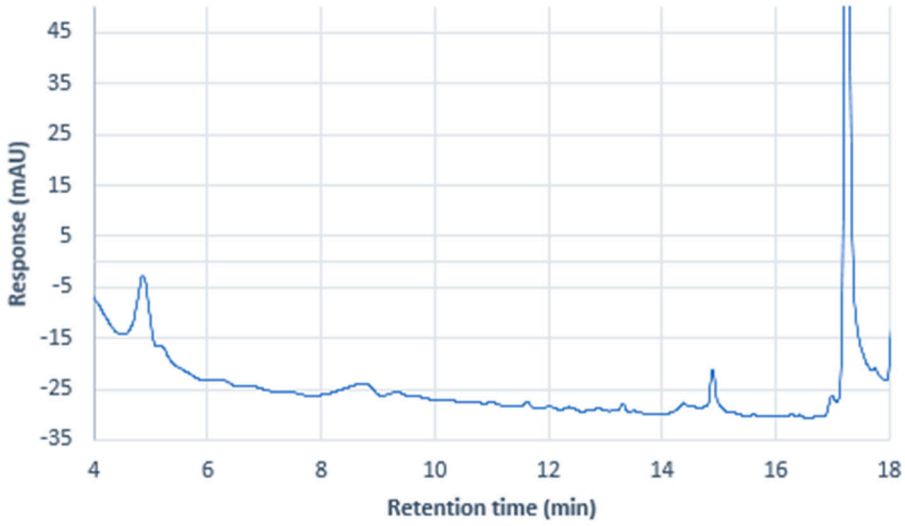


Figure S9. Chromatogram of a blank sample treated with the optimized procedure.