

## **Electronic supplementary information**

### **Using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) for investigations on single hair samples to solve the contamination versus incorporation issue of hair analysis in case of cocaine and methadone**

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**Table S1: Concentrations of the given analytes and concentration ratios of the given analytes/metabolites for the hair samples and if available for the wash solutions. Upper part: Results from the hair samples of the volunteers of the heavy contamination experiment. Bottom part: Results of from the routine hair samples with the given cocaine concentrations. Abbreviations: Bec, benzoylecgonine; CE, cocaethylene; Coc, cocaine; m-OH-Bec, meta hydroxybenzoylecgonine; m-OH-COC, meta hydroxycocaine; Noc, norcocaine; p-OH-Bec, para hydroxybenzoylecgonine; p-OHCOC, para-hydroxycocaine; seg, segment. Decision criteria for classification as consumption (from ref.8):  $Bec/Coc > 0.05$ ;  $Noc/Coc > 0.01$ ;  $pOHCoc/Coc > 0.001$ ;  $mOHCoc/Coc > 0.001$ ;  $pOHBec/Coc > 0.0002$ ;  $mOHBec/COC > 0.0002$ . According to this decision model, a sample is reported as positive and consistent with predominant cocaine use, if  $COC \geq 500$  pg/mg and at least two of the three criteria are fulfilled.**

**Volunteer1**

	hair							wash solution									
	conc. [pg/mg]							ratio				conc. [pg/mg]*			ratio		
	pOHCOC	mOHCOC	pOHBE	mOHBE	Coc	Bec	Noc	Bec/Coc	Noc/Coc	pOHCoc/Coc	mOHCoc/Coc	pOHBec/Coc	mOHBec/Coc	Coc	Bec	Noc	Noc/(Coc+Bec)
<b>before</b>	0	0	0	0	0	0	0							0	0	0	
<b>1 week after</b>	0.8	1.0	0.0	0.0	4'100	130	30	0.0317	0.0073	0.0002	0.0002	0.0000	0.0000	< LOQ (34)	< LOQ (4)	0.6	0.0158
<b>3 week after</b>	5	8	0.0	0.6	16'000	1'400	78	0.0875	0.0049	0.0003	0.0005	0.0000	0.0000	165	< LOQ (9.5)	2	0.0115
<b>8 week after</b>	10	17	1.4	1.6	13'000	1'300	82	0.1000	0.0063	0.0008	0.0013	0.0001	0.0001	58	10	1	0.0147

**Volunteer 2**

	hair							wash solution									
	conc. [pg/mg]							ratio				conc. [pg/mg]*			ratio		
	pOHCOC	mOHCOC	pOHBE	mOHBE	Coc	Bec	Noc	Bec/Coc	Noc/Coc	pOHCoc/Coc	mOHCoc/Coc	pOHBec/Coc	mOHBec/Coc	Coc	Bec	Noc	Noc/(Coc+Bec)
<b>before</b>	0	0	0	0	0	0	0							0	0	0	
<b>1 week after</b>	0.8	1.0	0	0	5'400	200	49	0.0370	0.0091	0.0001	0.0002	0.0000	0.0000	150	< LOQ (18)	2	0.0119
<b>3 week after</b>	0.6	0.6	0	0	2'200	140	9	0.0636	0.0041	0.0003	0.0003	0.0000	0.0000	168	< LOQ (8.5)	< LOQ (0.4)	0.0023
<b>8 week after</b>	0.6	0.7	0	0	810	60	3	0.0741	0.0037	0.0007	0.0009	0.0000	0.0000	< LOQ (11)	< LOQ (2.5)	< LOQ (0.25)	0.0185

\*LOQ: Coc = 50 pg/mg, Bec = 10 pg/mg, Noc = 0.5 pg/mg

hair sample with 100'000 pg cocaine per mg

	conc. [pg/mg]							ratio					
	pOHCOC	mOHCOC	pOHBE	mOHBE	Coc	Bec	Noc	Bec/Coc	Noc/Coc	pOHCoc/Coc	mOHCoc/Coc	pOHBeC/Coc	mOHBeC/Coc
Seg 1	140	190	27	8	101'000	7'700	1'100	0.0762	0.0109	0.0014	0.0019	0.0003	0.0001

hair sample with 180'000 pg cocaine per mg

	conc. [pg/mg]							ratio					
	pOHCOC	mOHCOC	pOHBE	mOHBE	Coc	Bec	Noc	Bec/Coc	Noc/Coc	pOHCoc/Coc	mOHCoc/Coc	pOHBeC/Coc	mOHBeC/Coc
Seg 1	240	460	88	42	174'000	23'000	3'000	0.1322	0.0172	0.0014	0.0026	0.0005	0.0002

hair sample with 10'000 pg cocaine per mg

	conc. [pg/mg]							ratio					
	pOHCOC	mOHCOC	pOHBE	mOHBE	Coc	Bec	Noc	Bec/Coc	Noc/Coc	pOHCoc/Coc	mOHCoc/Coc	pOHBeC/Coc	mOHBeC/Coc
Seg 1	21	26	4	2	10'200	760	140	0.0745	0.0137	0.0021	0.0025	0.0004	0.0002