

## Potential of desorption electrospray ionization and paper spray ionization with high-resolution mass spectrometry for the screening of sports doping agents in urine

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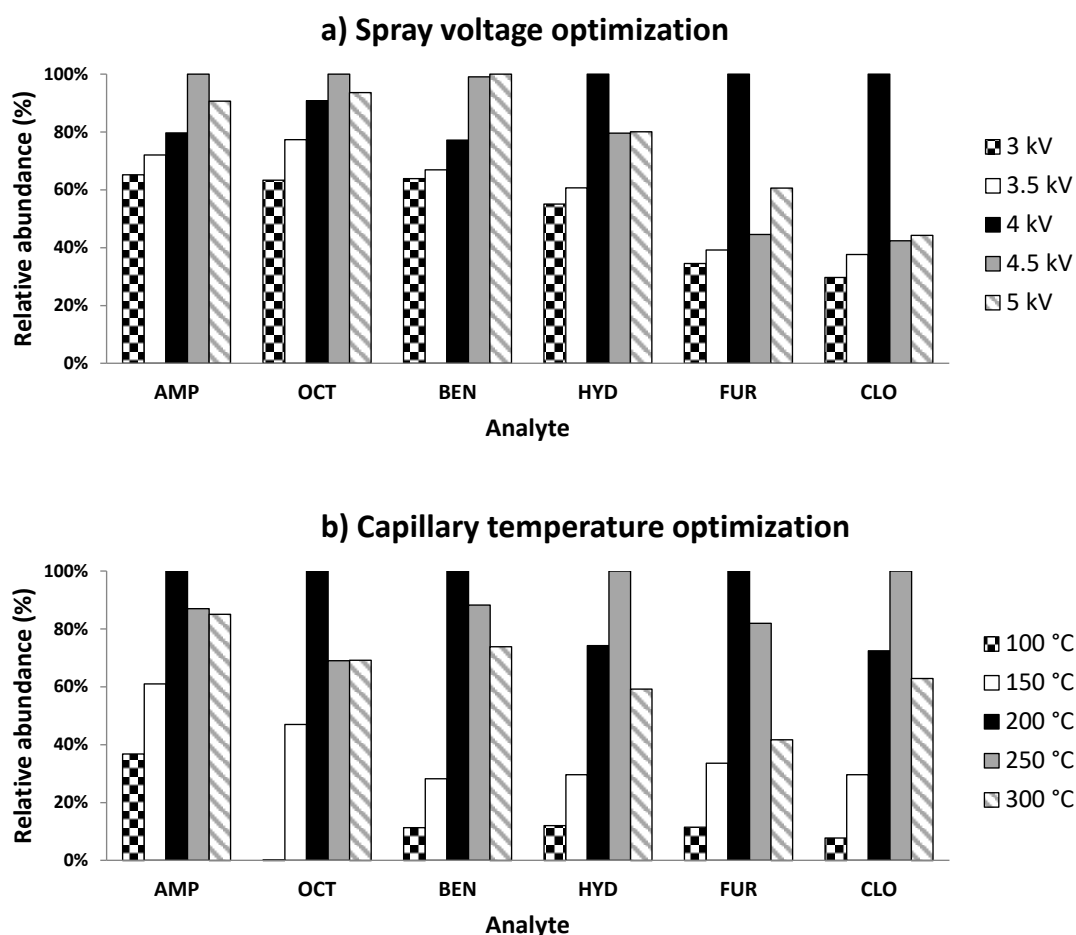
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## Supplementary Information

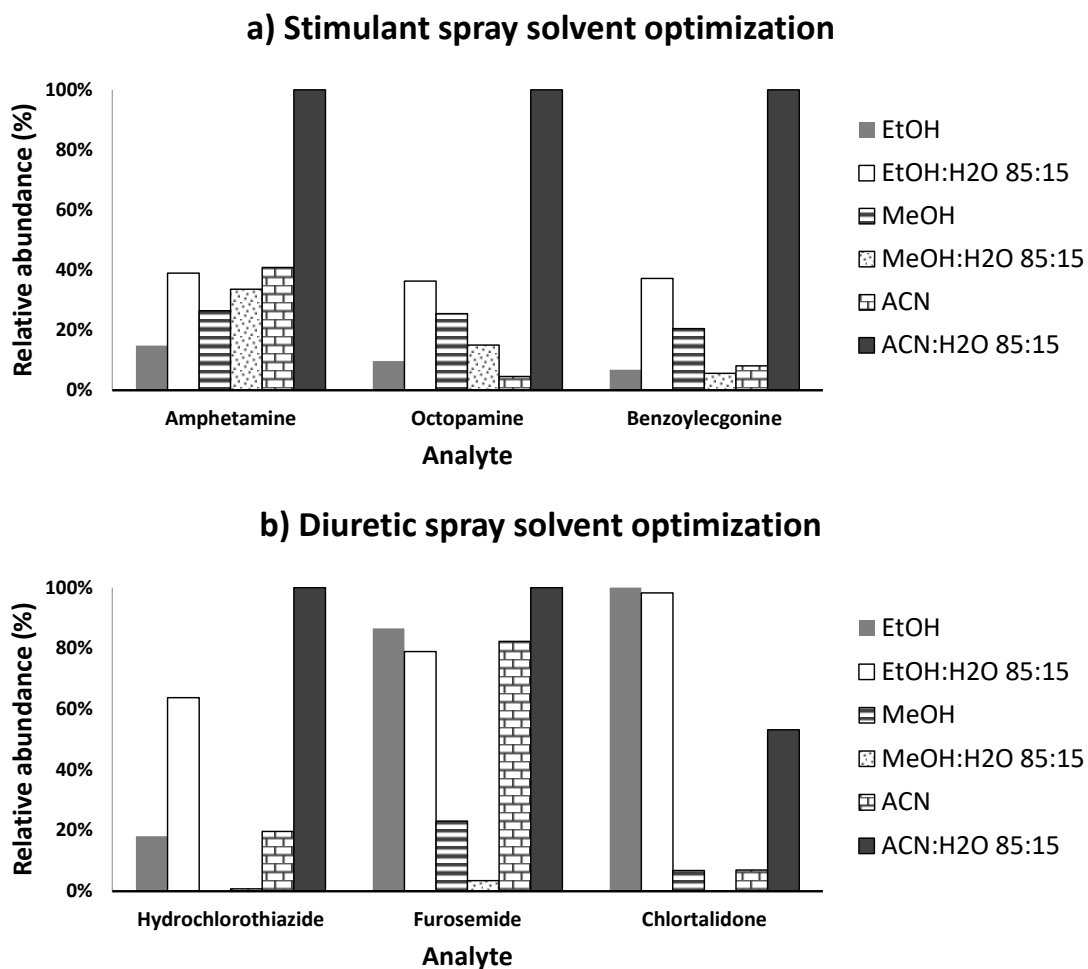
**Table S1.** Diagnostic ions used in full scan for screening all tested analytes in both DESI and PSI.

Stimulant	Formula	Diagnostic ions ( <i>m/z</i> and assignment)
amfepramone	C <sub>13</sub> H <sub>19</sub> NO	206.1539 [M+H] <sup>+</sup> ; 188,1434 [M+H-H <sub>2</sub> O] <sup>+</sup>
amiphenazole	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> S	192.0590 [M+H] <sup>+</sup>
amphetamine	C <sub>9</sub> H <sub>13</sub> N	136.1121 [M+H] <sup>+</sup> ; 119.0855 [M+H-NH <sub>3</sub> ] <sup>+</sup> ; 91.0542 [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup>
benfluorex	C <sub>19</sub> H <sub>20</sub> NO <sub>2</sub> F <sub>3</sub>	352.1519 [M+H] <sup>+</sup> ; 335.1254 [M+H-NH <sub>3</sub> ] <sup>+</sup>
benzoylecgonine	C <sub>16</sub> H <sub>19</sub> NO <sub>4</sub>	290.1387 [M+H] <sup>+</sup> ; 312.1206 [M+Na] <sup>+</sup>
benzphetamine	C <sub>17</sub> H <sub>21</sub> N	240.1747 [M+H] <sup>+</sup>
benzylpiperazine	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub>	177.1386 [M+H] <sup>+</sup>
caffeine	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	195.0877 [M+H] <sup>+</sup>
carphedon	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	219.1128 [M+H] <sup>+</sup>
chlorphentermine	C <sub>10</sub> H <sub>14</sub> NCl	184.0888 [M+H] <sup>+</sup> ; 148.1121 [M+H-HCl] <sup>+</sup>
clobenzorex	C <sub>16</sub> H <sub>18</sub> NCl	260.1201 [M+H] <sup>+</sup> ; 277.1466 [M+NH <sub>4</sub> ] <sup>+</sup>
cropropamide	C <sub>13</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub>	241.1911 [M+H] <sup>+</sup> ; 258.2176 [M+NH <sub>4</sub> ] <sup>+</sup>
crotetamide	C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	249.1574 [M+Na] <sup>+</sup> ; 265.1313 [M+K] <sup>+</sup> ; 227.1754 [M+H] <sup>+</sup>
cyclazodone	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	217.0972 [M+H] <sup>+</sup> ; 239.0791[M+Na] <sup>+</sup>
dobutamine	C <sub>18</sub> H <sub>23</sub> NO <sub>3</sub>	302.1751 [M+H] <sup>+</sup>
ephedrine	C <sub>10</sub> H <sub>15</sub> NO	166.1226 [M+H] <sup>+</sup> ; 148.1116 [M+H-H <sub>2</sub> O] <sup>+</sup>
etafedrine	C <sub>12</sub> H <sub>19</sub> NO	194.1539 [M+H] <sup>+</sup> ; 176.1434 [M+H-H <sub>2</sub> O] <sup>+</sup>
ethylamphetamine	C <sub>11</sub> H <sub>17</sub> N	164.1434 [M+H] <sup>+</sup>
famprofazone	C <sub>24</sub> H <sub>31</sub> N <sub>3</sub> O	378.2540 [M+H] <sup>+</sup>
fenbutrazate	C <sub>23</sub> H <sub>29</sub> NO <sub>3</sub>	368.2220 [M+H] <sup>+</sup>
fencamfamin	C <sub>15</sub> H <sub>21</sub> N	216.1747 [M+H] <sup>+</sup> ; 199.1481 [M+H-NH <sub>3</sub> ] <sup>+</sup>
fencamine	C <sub>20</sub> H <sub>28</sub> N <sub>6</sub> O <sub>2</sub>	385.2347 [M+H] <sup>+</sup> ; 407.2166 [M+Na] <sup>+</sup>
fenetylline	C <sub>18</sub> H <sub>23</sub> N <sub>5</sub> O <sub>2</sub>	342.1925 [M+H] <sup>+</sup>
fenfluramine	C <sub>12</sub> H <sub>16</sub> NF <sub>3</sub>	232.1308 [M+H] <sup>+</sup> ; 249.1573 [M+NH <sub>4</sub> ] <sup>+</sup>
fenproporex	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub>	189.1386 [M+H] <sup>+</sup> ; 172.1121[M+H-NH <sub>3</sub> ] <sup>+</sup>
furfenorex	C <sub>15</sub> H <sub>19</sub> NO	230.1539 [M+H] <sup>+</sup>
heptaminol	C <sub>8</sub> H <sub>19</sub> NO	146.1539 [M+H] <sup>+</sup> ;128.1434 [M+H-H <sub>2</sub> O] <sup>+</sup>
isometheptene	C <sub>9</sub> H <sub>19</sub> N	142.1590 [M+H] <sup>+</sup>
MDEA	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub>	208.1332 [M+H] <sup>+</sup>
MDMA	C <sub>11</sub> H <sub>15</sub> NO <sub>2</sub>	194.1176 [M+H] <sup>+</sup> ; 163.0748 [M+H-CH <sub>3</sub> NH <sub>2</sub> ] <sup>+</sup>
mefenorex	C <sub>12</sub> H <sub>18</sub> NCl	212.1201 [M+H] <sup>+</sup> ; 176.1434 [M+H-HCl] <sup>+</sup>
mephentermine	C <sub>11</sub> H <sub>17</sub> N	164.1434 [M+H] <sup>+</sup>
methamphetamine(d-)	C <sub>10</sub> H <sub>15</sub> N	150.1277 [M+H] <sup>+</sup>
methoxyphenamine	C <sub>11</sub> H <sub>17</sub> NO	180.1383 [M+H] <sup>+</sup>
methylephedrine	C <sub>11</sub> H <sub>17</sub> NO	180.1383 [M+H] <sup>+</sup> ; 162.1277 [M+H-H <sub>2</sub> O] <sup>+</sup>
methylhexaneamine	C <sub>7</sub> H <sub>17</sub> N	116.1434 [M+H] <sup>+</sup>
nikethamide	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O	179.1179 [M+H] <sup>+</sup> ;196.1444 [M+NH <sub>4</sub> ] <sup>+</sup>
norfenfluramine	C <sub>10</sub> H <sub>12</sub> NF <sub>3</sub>	204.0995 [M+H] <sup>+</sup>
norpseudoephedrine	C <sub>9</sub> H <sub>13</sub> NO	152.1070 [M+H] <sup>+</sup> ; 134.0964 [M+H-H <sub>2</sub> O] <sup>+</sup> ; 135.0804 [M+H-NH <sub>3</sub> ] <sup>+</sup>
octopamine	C <sub>8</sub> H <sub>11</sub> NO <sub>2</sub>	136.0757 [M+H-H <sub>2</sub> O] <sup>+</sup> ; 154.0863 [M+H] <sup>+</sup>
phenmetrazine	C <sub>11</sub> H <sub>15</sub> NO	178.1226 [M+H] <sup>+</sup>
phentermine	C <sub>10</sub> H <sub>15</sub> N	150.1277 [M+H] <sup>+</sup> ; 133.1012 [M+H-NH <sub>3</sub> ] <sup>+</sup>

<i>p</i> -Hydroxyamphetamine	C <sub>9</sub> H <sub>13</sub> NO	152.1070 [M+H] <sup>+</sup> ; 134.0964 [M+H-H <sub>2</sub> O] <sup>+</sup>
<i>p</i> -Hydroxymetamphetamine	C <sub>10</sub> H <sub>15</sub> NO	166.1226 [M+H] <sup>+</sup>
pipradol	C <sub>18</sub> H <sub>21</sub> NO	268.1696 [M+H] <sup>+</sup> ; 250.1590 [M+H-H <sub>2</sub> O] <sup>+</sup>
<i>p</i> -Methylamphetamine	C <sub>10</sub> H <sub>15</sub> N	150.1277 [M+H] <sup>+</sup>
prenylamine	C <sub>24</sub> H <sub>27</sub> N	330.2216 [M+H] <sup>+</sup>
prolintane	C <sub>15</sub> H <sub>23</sub> N	218.1903 [M+H] <sup>+</sup>
propylhexedrine	C <sub>10</sub> H <sub>21</sub> N	156.1747 [M+H] <sup>+</sup>
sibutramine	C <sub>17</sub> H <sub>26</sub> NCl	280.1827 [M+H] <sup>+</sup> ; 244.2060 [M+H-HCl] <sup>+</sup> ; 302.1646 [M+Na] <sup>+</sup>
strychnine	C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	335.1754 [M+H] <sup>+</sup>
tuaminoheptane	C <sub>7</sub> H <sub>17</sub> N	116.1434 [M+H] <sup>+</sup>
<b>Diuretic</b>	<b>Formula</b>	<b>Diagnostic ions (<i>m/z</i> and assignment)</b>
chlortalidone	C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> ClS	337.0055 [M-H] <sup>-</sup> ; 372.9822 [M+Cl] <sup>-</sup>
furosemide	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>5</sub> ClS	329.0004 [M-H] <sup>-</sup>
hydrochlorothiazide	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>4</sub> ClS <sub>2</sub>	295.9572 [M-H] <sup>-</sup> ; 331.9339 [M+Cl] <sup>-</sup>



**Figure S1:** Optimization of a) the spray voltage and b) the capillary temperature in DESI-HRMS for three stimulants and three diuretics: amphetamine (AMP), octopamine (OCT), benzoylecgonine (BEN), hydrochlorothiazide (HYD), furosemide (FUR) and chlortalidone (CLO)



**Figure S2:** Effect of the spray solvent composition in the PSI ion abundances of selected a) stimulants and b) diuretics

**Table S2:** Optimum spray voltages set for the pure solvents and for the hydro-organic mixtures tested in PSI. The optimization was performed in both positive and negative modes.

	<b>PSI (+)</b>	<b>PSI (-)</b>
<b>Solvent</b>	<b>Voltage (kV)</b>	<b>Voltage (kV)</b>
MeOH:H <sub>2</sub> O 85:15	3	3
EtOH:H <sub>2</sub> O 85:15	3.5	3
ACN:H <sub>2</sub> O 85:15	4.5	3
MeOH	3	3.5
EtOH	3	3
ACN	4.5	4