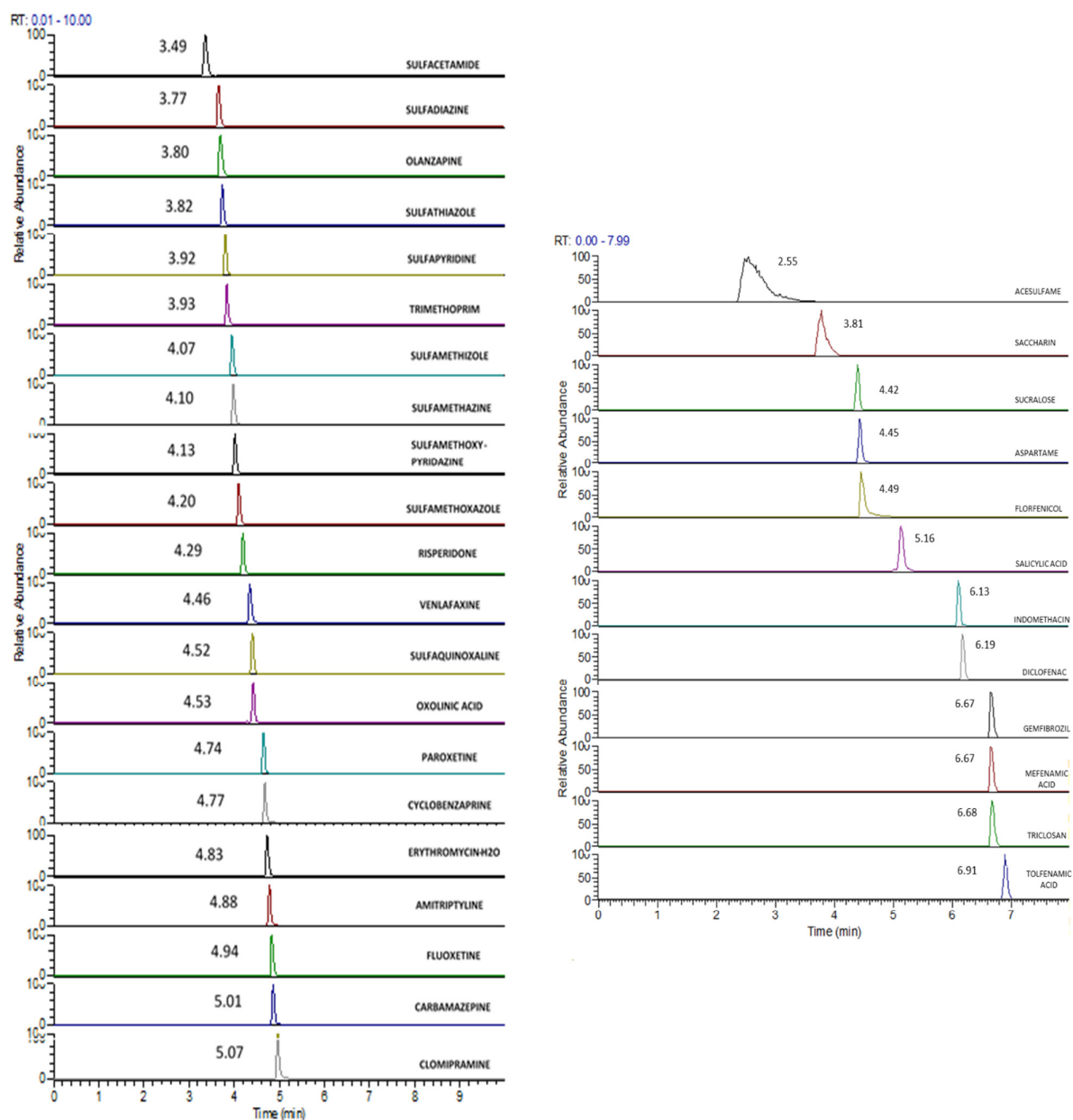


Supplementary Materials

# Magnetic Solid-Phase Extraction Based on Silica and Graphene Materials for Sensitive Analysis of Emerging Contaminants in Wastewater with the aid of UHPLC-Orbitrap-MS

**Table S1.** Selection of magnetic sorbents for the extraction of investigated analytes.

Compounds	MSPE Fe <sub>3</sub> O <sub>4</sub> @GO	MSPE Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @C18
Acesulfame	✓	
Amitriptyline		✓
Aspartame	✓	
Carbamazepine	✓	✓
Clomipramine		✓
Cyclobenzaprine		✓
Diclofenac		✓
Erythromycin-H <sub>2</sub> O		✓
Florfenicol	✓	
Fluoxetine		✓
Gemfibrozil	✓	
Indomethacin		✓
Mefenamic acid		✓
Olanzapine		✓
Oxolinic acid	✓	
Paroxetine		✓
Risperidone		✓
Saccharin	✓	
Salicylic acid	✓	
Sucralose	✓	
Sulfacetamide	✓	
Sulfadiazine	✓	
Sulfamethazine	✓	
Sulfamethizole	✓	
Sulfamethoxazole	✓	
Sulfamethoxy-pyridazine	✓	
Sulfapyridine	✓	
Sulfaquinoxaline	✓	
Sulfathiazole	✓	
Tolfenamic acid		✓
Triclosan		✓
Trimethoprim	✓	✓
Venlafaxine		✓



**Figure S1.** Extracted Ion Chromatogram, XIC of standard solution of 5 µg/L in UHPLC-LTQ/Orbitrap of target analytes a) positive ionization, b) negative ionization.

**Table S2.** Parameters for full MS/dd-MS<sup>2</sup> Orbitrap analysis (Positive Ionization).

COMPOUND	Rt(min)	Elemental formula	Theoretical mass (m/z)	Empirical mass (m/z)	RDB	Δ (ppm)	IQL (µg/L-1)	FRAGM. ION	ELE-MENTAL FORMULA	NCE
Sulfacetamide	3.49	C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> S <sup>+</sup>	215.0485	215.0486	4.5	0.514	0.44	108.0448	C <sub>6</sub> HNO <sup>+</sup>	30
								92.0500	C <sub>6</sub> H <sub>6</sub> N <sup>+</sup>	
								156.0112	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S <sup>+</sup>	
Sulfadiazine	3.77	C <sub>10</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> S <sup>+</sup>	251.0597	251.0598	7.5	0.307	0.22	156.0112	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S <sup>+</sup>	30
								92.0489	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S <sup>+</sup>	
								256.0902	C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> S <sup>+</sup>	
Olanzapine	3.80	C <sub>17</sub> H <sub>21</sub> N <sub>4</sub> S <sup>+</sup>	313.1481	313.1481	9.5	-0.140	0.23	230.0745	C <sub>12</sub> H <sub>12</sub> N <sub>3</sub> S <sup>+</sup>	35
								156.0112	C <sub>6</sub> HNO <sub>2</sub> S <sup>+</sup>	
								108.0440	C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup>	
Sulfathiazole	3.82	C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> S <sup>+</sup>	256.0209	256.0211	6.5	0.021	0.24	156.0112	C <sub>6</sub> HNO <sub>2</sub> S <sup>+</sup>	30
								108.0440	C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup>	
								156.0112	C <sub>6</sub> HNO <sub>2</sub> S <sup>+</sup>	
Sulfapyridine	3.92	C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> S <sup>+</sup>	250.0645	250.0645	7.5	0.105	0.07	108.0440	C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup>	30
								156.0112	C <sub>6</sub> HNO <sub>2</sub> S <sup>+</sup>	
								108.0440	C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup>	

Trimethoprim	3.93	C <sub>14</sub> H <sub>19</sub> N <sub>4</sub> O <sub>3</sub> <sup>+</sup>	291.1452	291.1453	7.5	0.457	0.18	184.0867 230.1161 261.0980 156.0113	C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> <sup>+</sup> C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sup>+</sup> C <sub>12</sub> H <sub>13</sub> N <sub>4</sub> O <sub>3</sub> <sup>+</sup> C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup>	30
Sulfamethizole	4.07	C <sub>9</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> <sup>+</sup>	271.0318	271.0319	6.5	0.393	0.17	108.0447 65.0393 92.050	C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup> C <sub>5</sub> H <sub>5</sub> <sup>+</sup> C <sub>6</sub> H <sub>6</sub> N <sup>+</sup>	35
Sulfamethazine	4.10	C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> S <sup>+</sup>	279.0910	279.0909	7.5	-0.441	0.16	123.0662	C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> <sup>+</sup>	30
Sulfamethoxy-pyridazine	4.13	C <sub>11</sub> H <sub>13</sub> N <sub>4</sub> O <sub>3</sub> S <sup>+</sup>	281.0703	281.0703	7.5	0.045	0.23	156.0113 108.0430 92.0486	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S <sup>+</sup> C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup> C <sub>6</sub> H <sub>6</sub> N <sup>+</sup>	20

Table S2. Parameters for full MS/dd-MS<sup>2</sup> Orbitrap analysis, (continued).

COMPOUND	Rt(min)	Elemental formula	Theoretical mass (m/z)	Empirical mass (m/z)	RDB	Δ (ppm)	IQL (μg/L-1)	FRAGM. ION	ELE-MENTAL FORMULA	NCE
Sulfamethoxazole	4.20	C <sub>10</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> S <sup>+</sup>	254.0594	254.0592	6.5	-0.742	0.22	188.0818 156.0113 147.0789	C <sub>10</sub> H <sub>10</sub> N <sub>3</sub> O <sup>+</sup> C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S <sup>+</sup> C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> <sup>+</sup>	20
Risperidone	4.29	C <sub>23</sub> H <sub>28</sub> FN <sub>4</sub> O <sub>2</sub> <sup>+</sup>	411.2191	411.2190	11.5	-0.197	0.44	191.1171	C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sup>+</sup>	35
Venlafaxine	4.46	C <sub>17</sub> H <sub>28</sub> NO <sub>2</sub> <sup>+</sup>	278.2115	278.2117	4.5	0.878	0.42	121.0643 260.2006	C <sub>8</sub> H <sub>9</sub> O <sup>+</sup> C <sub>17</sub> H <sub>26</sub> NO <sup>+</sup>	25
Sulfaquinoxaline	4.52	C <sub>14</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> S <sup>+</sup>	301.0754	301.0754	10.5	0.090	0.44	156.0113 108.0440	C <sub>6</sub> HNO <sub>2</sub> S <sup>+</sup> C <sub>6</sub> H <sub>6</sub> NO <sup>+</sup>	30
Oxolinic Acid	4.53	C <sub>13</sub> H <sub>12</sub> NO <sub>5</sub> <sup>+</sup>	262.0710	262.0709	8.5	-0.378	0.07	244.1905	C <sub>13</sub> H <sub>10</sub> NO <sub>4</sub> <sup>+</sup>	25
Paroxetine	4.74	C <sub>19</sub> H <sub>21</sub> O <sub>3</sub> NF <sup>+</sup>	330.1500	330.1502	9.5	0.611	0.06	192.1180 151.0387	C <sub>12</sub> H <sub>15</sub> NF <sup>+</sup> C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> <sup>+</sup>	35
Cyclobenzaprine	4.77	C <sub>20</sub> H <sub>22</sub> N <sup>+</sup>	276.1747	276.1749	10.5	0.810	0.16	58.0659 84.0814	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup> C <sub>5</sub> H <sub>10</sub> N <sup>+</sup>	30
Erythromycin-H <sub>2</sub> O	4.83	C <sub>37</sub> H <sub>66</sub> NO <sub>12</sub>	716.4580	716.4591	5.5	1.601	0.14	158.1175 558.3635 233.1322	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> N <sup>+</sup> C <sub>26</sub> H <sub>54</sub> O <sub>12</sub> C <sub>8</sub> H <sub>17</sub> <sup>+</sup>	40
Amitriptyline	4.88	C <sub>20</sub> H <sub>24</sub> N <sup>+</sup>	278.1903	278.1905	9.5	0.624	0.09	191.0854 155.0854 117.0695	C <sub>15</sub> H <sub>11</sub> <sup>+</sup> C <sub>12</sub> H <sub>11</sub> <sup>+</sup> C <sub>9</sub> H <sub>9</sub> <sup>+</sup>	30
Fluoxetine	4.94	C <sub>17</sub> H <sub>19</sub> F <sub>3</sub> NO <sup>+</sup>	310.1413	310.1415	7.5	0.563	0.06	148.1119 247.0918 194.0964	C <sub>10</sub> H <sub>14</sub> N <sup>+</sup> C <sub>4</sub> H <sub>18</sub> FN <sub>3</sub> <sup>+</sup> C <sub>14</sub> H <sub>12</sub> N <sup>+</sup>	15
Carbamazepine	5.01	C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O	237.1022	237.1024	10.5	0.677	0.16	220.0756 192.0808	C <sub>15</sub> H <sub>10</sub> NO <sup>+</sup> C <sub>14</sub> H <sub>10</sub> N <sup>+</sup>	35
Clomipramine	5.07	C <sub>19</sub> H <sub>24</sub> ClN <sub>2</sub> <sup>+</sup>	315.1623	315.1627	8.5	1.418	0.10	86.0940 58.059	C <sub>3</sub> H <sub>12</sub> N <sup>+</sup> C <sub>3</sub> H <sub>8</sub> N <sup>+</sup>	30

Table S3. Parameters for full MS/dd-MS<sup>2</sup> Orbitrap analysis (Negative Ionization).

COMPOUND	Rt(min)	Elemental formula	Theoretical mass (m/z)	Empirical mass (m/z)	RDB	Δ (ppm)	IDL (μg/L-1)	IQL (μg/L-1)	FRAGM. ION	ELEMENTAL FORMULA	NCE
Acesulfame	2.55	C <sub>4</sub> H <sub>4</sub> NO <sub>4</sub> S <sup>-</sup>	161.9867	161.9868	3.5	0.916	0.94	3.13	77.9642 82.0285	NO <sub>2</sub> S <sup>-</sup> C <sub>4</sub> H <sub>4</sub> NO <sup>-</sup>	30
Saccharin	3.79	C <sub>7</sub> H <sub>4</sub> NO <sub>3</sub> S <sup>-</sup>	181.9917	181.9919	6.5	0.896	0.07	0.24	105.9592 61.9693	CNO <sub>3</sub> S <sup>-</sup> NOS <sup>-</sup>	30
Sucralose	4.41	C <sub>12</sub> H <sub>18</sub> Cl <sub>3</sub> O <sub>8</sub> <sup>-</sup>	395.0073	395.0072	2.5	-0.187	0.19	0.63	359.0299	C <sub>12</sub> H <sub>17</sub> Cl <sub>3</sub> O <sub>8</sub>	30
Aspartame	4.44	C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O <sub>5</sub> <sup>-</sup>	293.1143	293.1141	7.5	-0.665	0.07	0.24	261.0880	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> <sup>-</sup>	15
Florfenicol	4.47	C <sub>12</sub> H <sub>13</sub> Cl <sub>2</sub> FNO <sub>4</sub> S <sup>-</sup>	355.9932	355.9936	5.5	1.164	0.02	0.06	335.9869 218.9890	C <sub>12</sub> H <sub>12</sub> Cl <sub>2</sub> NO <sub>4</sub> S <sup>-</sup> C <sub>8</sub> H <sub>8</sub> ClO <sub>3</sub> S <sup>-</sup>	35
Salicylic acid	5.14	C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> <sup>-</sup>	137.0244	137.0250	5.5	4.252	0.05	0.16	93.00334 65.0384	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup> C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	30
Indomethacin	6.12	C <sub>19</sub> H <sub>15</sub> ClNO <sub>4</sub> <sup>-</sup>	356.0659	356.0675	12.5	-2.281	0.30	0.91	312.0796	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> Cl <sup>-</sup>	35
Diclofenac	6.19	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> NO <sub>2</sub> <sup>-</sup>	294.0094	294.0089	9.5	-1.725	0.22	0.74	250.0193	C <sub>13</sub> H <sub>10</sub> Cl <sub>2</sub> N <sup>-</sup>	35
Gemfibrozil	6.67	C <sub>15</sub> H <sub>21</sub> O <sub>3</sub> <sup>-</sup>	249.1496	249.1489	5.5	-2.881	0.38	1.25	121.0659	C <sub>8</sub> H <sub>9</sub> O <sup>-</sup>	25
Mefenamic Acid	6.67	C <sub>15</sub> H <sub>14</sub> NO <sub>2</sub> <sup>-</sup>	240.103	240.1026	9.5	-1.674	0.07	0.23	196.1133 240.1029	C <sub>14</sub> H <sub>14</sub> N <sup>-</sup> C <sub>15</sub> H <sub>14</sub> NO <sub>2</sub> <sup>-</sup>	20
Triclosan	6.68	C <sub>12</sub> H <sub>6</sub> Cl <sub>3</sub> O <sub>2</sub> <sup>-</sup>	286.9439	286.9433	8.5	-2.042	0.18	0.59	161.2632	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> O <sup>-</sup>	25
Tolfenamic Acid	6.91	C <sub>14</sub> H <sub>11</sub> ClNO <sub>2</sub> <sup>-</sup>	260.0484	260.0480	9.5	-1.460	0.23	0.77	216.0580	C <sub>14</sub> H <sub>11</sub> ClNO <sub>2</sub> <sup>-</sup>	20

\* Rt: Retention time; IDL: Instrumental Detection Limit.

**Table S4.** LogP parameter of target analytes.

Compounds	logP
Acesulfame	-0.552
Amitriptyline	4.810
Aspartame	-2.218
Carbamazepine	2.766
Clomipramine	4.883
Cyclobenzaprine	4.613
Diclofenac	4.259
Erythromycin	2.596
Florfenicol	0.670
Fluoxetine	4.173
Gemfibrozil	4.387
Indomethacin	3.530
Mefenamic acid	5.398
Olanzapine	3.388
Oxolinic acid	1.353
Paroxetine	3.148
Risperidone	2.628
Saccharin	0.449
Salicylic acid	1.977
Sucralose	-0.465
Sulfacetamide	-0.300
Sulfadiazine	0.387
Sulfamethazine	0.650
Sulfamethizole	0.214
Sulfamethoxazole	0.791
Sulfamethoxy-pyridazine	0.466
Sulfapyridine	1.009
Sulfaquinoxaline	1.552
Sulfathiazole	0.975
Tolfenamic acid	5.488
Triclosan	4.982
Trimethoprim	1.284
Venlafaxine	2.739

Data concerning obtained from international database <https://chemaxon.com/>.