Supplemental Section

Figure S1. Analytical resolution of 26DM (quantitation ion peak), as compared between injections made on a DB-17MS (top chromatogram) and a DB-FFAP (bottom chromatogram) analytical column. In each chromatogram, 26DM analyte peak is labeled with an asterisk.

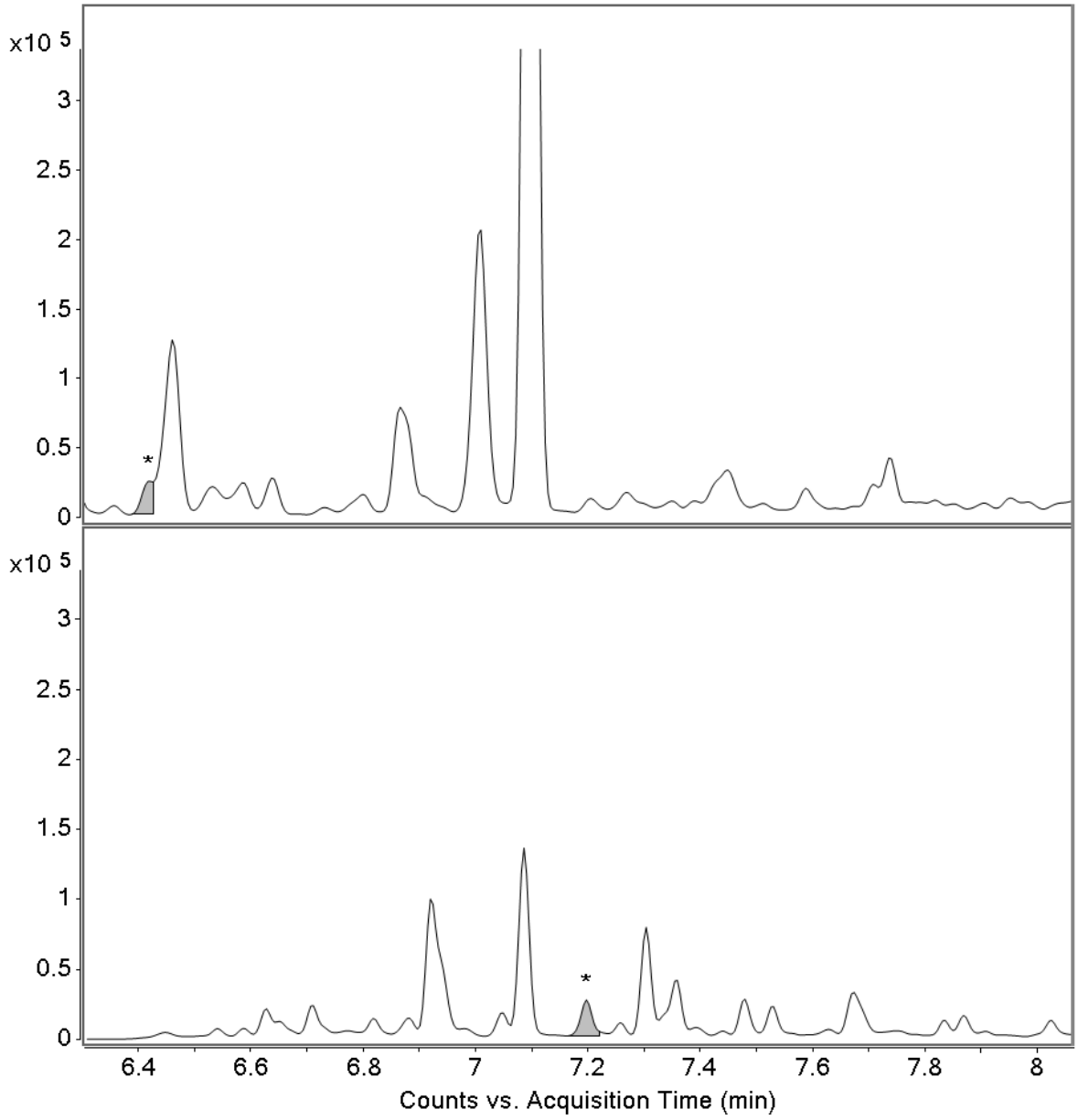

Table S1: Instrument operation parameters and settings.

Agilent 7890A, 7890B		Agilent 7000C	
Instrument operation parameters	Setting	Instrument operation parameters	Setting
Injection port	Pulsed splitless	MSD mode	Positive ion detection
Injection port temperature	250ºC	Ionization mode	Electron impact
Injection volume	1 µL	Source temperature	280ºC
Injection pulse pressure	30 psi until 0.35 min	Quad temperature	150ºC
Septum purge flow	3 mL/min	Collision gas	N_2 at 1.5 mL/min
Purge flow to split vent	60 mL/min at 0.35 min	Collision pressure	35 psi
Column 1	Constant flow 1.68 ± 0.05 mL/min (analytical run) Constant flow -2.20 ± 0.05 mL/min (post-run)	Quench gas	He at 2.25 mL/min
Column 2	Constant flow 1.85 ± 0.05 mL/min (analytical run) Constant flow 10.5 ± 0.05 mL/min (post-run)	Detector gain	20 (x 10^5)
MSD transfer line temperature	280ºC		
Oven program (analytical run)	80ºC (hold 2 min) 30ºC/min ramp to 180ºC 15ºC/min ramp to 240ºC		
Oven program (post-run)	240ºC (hold 5.5 min)		

Table S2: Compound-dependent MS parameters and ion transitions for AA analysis.

Analyte		Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (*V*)	Dwell time (*ms*)
OTOL	Quantitation ion	253	116	30	55
	Confirmation ion	253	106	25	17
	Internal standard, quantitation ion	259	122	30	35
	Internal standard, confirmation ion	259	112	25	35
26DM	Quantitation ion	267	148	10	65
	Confirmation ion	267	120	25	65
	Internal standard, quantitation ion	273	154	15	65
	Internal standard, confirmation ion	273	126	30	65
OANS	Quantitation ion	269	135	30	35
	Confirmation ion	269	190	15	55
	Internal standard, quantitation ion	276	139	35	35
	Internal standard, confirmation ion	276	157	15	35
1AMN	Quantitation ion	289	144	20	45
	Confirmation ion	289	127	30	45
	Internal standard, quantitation ion	295	150	20	45
	Internal standard, confirmation ion	296	151	20	45
2AMN	Quantitation ion	289	144	20	45
	Confirmation ion	289	127	30	45
	Internal standard, quantitation ion	296	151	20	45
	Internal standard, confirmation ion	295	150	20	45
4ABP	Quantitation ion	315.1	170	30	65
	Confirmation ion	315.1	141	40	65
	Internal standard, quantitation ion	324	179	20	65
	Internal standard, confirmation ion	324	150	45	65

Table S3: Sample processing and instrument parameters were varied from method conditions to test the ruggedness of assay. Three different column lots were tested to assess the ruggedness of the DB-FFAP column.

Analyte	Measured concentration (ng/L)															
	3 µL PFPA, control	2 uL PFPA (%-diff)	4 uL PFPA (%-diff)	15 hr hydrolysis, control	14 hr hydrolysis (%-diff)	16 hr hydrolysis (%-diff)	250°C inlet temperature, control	240°C inlet temperature (%-diff)	260°C inlet temperature (%-diff)	30 psi pulsed pressure, control	25 psi pulsed pressure (%-diff)	35 psi pulsed pressure (%-diff)	Column lot #1	Column lot #2 (%-diff)	Column lot #1	Column lot #3 (%-diff)
OTOL	448.1	515.9 (15.12)	441.8 (-1.40)	448.1	460.4 (2.73)	513.1 (14.49)	214.7	219.0 (2.02)	203.4 (-5.27)	214.7	181.2 (-15.61)	215.1 (0.20)	345.9	341.9 (-1.16)	170.8	154.0 (-9.83)
													600.0	527.9 (-12.78)	488.1	490.5 (0.49)
													842.4	884.8 (4.92)	64.4	73.9 (14.65)
													431.4	466.6 (7.84)	159.4	168.4 (5.62)
													750.1	753.3 (0.42)	491.4	562.5 (14.46)
26DM	456.0	413.9 (-9.23)	419.6 (-7.98)	456.0	435.1 (-4.60)	411.6 (-9.74)	150.7	149.1 (-1.02)	154.7 (2.65)	150.7	156.2 (3.67)	152.3 (1.09)	139.2	146.6 (5.13)	108.6	113.4 (4.40)
													281.2	319.4 (12.72)	445.1	495.8 (11.39)
													192.7	212.7 (9.90)	17.7	19.5 (10.20)
													66.2	66.7 (0.75)	112.8	120.3 (6.70)
													221.6	216.8 (-2.21)	454.6	474.4 (4.36)
OANS	403.4	391.9 (-2.86)	375.2 (-7.00)	403.4	398.6 (-1.20)	389.2 (-3.52)	133.6	139.4 (4.33)	138.2 (3.49)	133.6	141.3 (5.81)	151.3 (13.27)	125.8	125.2 (-0.45)	147.1	143.8 (-2.24)
													345.2	345.6 (0.13)	475.8	474.1 (-0.35)
													307.6	295.9 (-3.89)	41.8	43.3 (3.50)
													63.5	64.3 (1.36)	143.7	145.9 (1.51)
													290.4	300.7 (3.49)	462.4	471.2 (1.90)
1AMN	314.9	295.4 (-6.21)	311.7 (-1.02)	314.9	319.3 (1.39)	287.7 (-8.64)	97.9	106.8 (9.15)	98.6 (0.71)	97.9	98.8 (0.96)	100.7 (2.87)	40.7	37.3 (-8.81)	102.5	97.1 (-5.27)
													40.9	38.4 (-6.46)	433.6	415.1 (-4.26)
													60.0	58.5 (-2.52)	13.0	13.4 (3.01)
													23.9	21.8 (-9.28)	99.9	99.0 (-0.97)
													22.7	21.9 (-3.45)	419.9	378.9 (-9.78)
2AMN	315.8	309.5 (-2.00)	308.2 (-2.43)	315.8	312.8 (-0.95)	311.3 (-1.44)	93.0	101.7 (9.37)	91.2 (-1.89)	93.0	92.0 (-1.08)	92.9 (-0.07)	10.4	10.3 (-1.19)	108.3	102.6 (-5.31)
													317.7	309.5 (-2.62)	442.9	434.2 (-1.97)
													497.5	488.7 (-1.78)	15.0	15.7 (4.60)
													16.8	16.5 (-1.54)	102.6	98.6 (-3.90)
													396.1	393.5 (-0.66)	436.5	424.8 (-2.69)
4ABP	337.0	335.9 (-0.32)	334.3 (-0.78)	337.0	344.6 (2.26)	335.7 (-0.38)	105.6	119.5 (13.20)	112.9 (6.91)	105.6	114.1 (8.10)	118.4 (12.17)	24.8	24.4 (-1.72)	413.5	444.1 (7.42)
													267.8	271.8 (1.49)	5.2	5.4 (3.96)
													339.7	332.4 (-2.17)	52.5	61.3 (16.75)
													21.6	21.6 (0.24)	105.6	111.7 (5.75)
													283.5	283.7 (0.08)	405.2	405.7 (0.14)

Table S4: Characterization statistics obtained for QC low and high pools, using 39 replicates from each pool.

Analyte	QC low pool, averaged concentration (ng/L)	CV	QC high pool, averaged concentration (ng/L)	CV
OTOL	150.7	8.76	485.9	6.44
26DM	121.29	7.80	502.6	4.22
OANS	153.4	2.74	505.8	4.33
1AMN	110.8	5.56	458.1	5.11
2AMN	111.7	5.27	479.8	5.01
4ABP	109.0	4.04	446.1	5.24