

**Ionization Efficiency for Environmentally Relevant Compounds
Using Atmospheric Pressure Photoionization Versus Electrospray Ionization**

Prakriya Shrestha, Katherine A. Maloof, Alayna Stephens, Clayton P. Donald, and Kevin R. Tucker
Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL

Supplemental Information

S1: Available analytes and internal standards		
Parameters	ESI	APPI
Fragmentor (V)	135	135
Collision energy (V)	0	0
Cell accelerator voltage (V)	4	4
Gas temperature (° C)	300	325
Vaporizer (° C)	-	350
Gas flow (L/min)	5	7
Nebulizer (psi)	45	40
Sheath gas temp (° C)	250	-
Sheath gas flow (L/min)	11	-

S2: Synthetic wastewater matrix preparation reagent and concentration		
Reagents	Concentration (M)	Weight Taken (g/L)
Potassium phosphate monobasic	0.00012	0.0186
Sodium acetate trihydrate	0.0099	1.3628
Magnesium sulfate heptahydrate	0.00009738	0.0259
Ammonium chloride	0.00179	0.0964
Calcium chloride dihydrate	0.000016	0.0027

S3: HPLC parameters for sample analysis		
HPLC Parameters	(+) ESI	(+) APPI
Column	No column (direct injection mode)	No column (direct injection mode)
Injection volume	5 µ L	10 µ L
Mobile phase	50% acetonitrile with 0.1% formic acid	Acetonitrile with 0.1% toluene
Mobile phase flow rate	0.200 mL/min	0.200 mL/min

S4: Optimized MS parameters for antibiotics precursor ion (ESI)						
Class	Compound	Molecular Weight (g)	Frag (V)	CAV (V)	Temp (°C)	Gas Flow (L/min)
Beta Lactam	Ampicillin	350.1	50	4	320	9
	Ceftriaxone	555.1	50	3	220	9
	Cephalexin	348.1	50	3	350	8
	Penicillin G	335.1	150	3	260	13
Macrolides	Erythromycin	734.5	130	3	280	8
	Tylosin	916.5	200	3	340	6
Sulfonamides	Sulfamethoxazole	254.1	80	3	300	6
	Trimethoprim	291.1	100	3	220	9
Tetracyclines	Oxytetracycline	461.2	50	3	280	9
	Tetracycline	445.2	80	3	300	11
Nitroimidazole	Metronidazole	172.1	65	3	230	9
	1,2 dimethyl-5-nitroimidazole	142.1	50	3	200	9

S5: Optimized MS parameters for EDCs precursor ion (ESI)						
Class	Compound	Molecular Weight (g)	Frag (V)	CAV (V)	Temp (°C)	Gas Flow (L/min)
Beta blockers	Propranolol	260.2	100	3	200	13
	Metoprolol	268.2	50	7	320	8
	Acebutolol	337.2	80	3	350	8
	Atenolol	267.2	100	3	320	8
Selective serotonin reuptake inhibitor	Venlafaxine	278.2	80	5	280	9
	Citalopram	325.2	100	5	320	8
	Paroxetine	330.2	100	4	350	12

S6: Optimized MS parameters for antibiotics precursor ion (APPI)						
Class	Compound	Frag (V)	CAV (V)	Temp (°C)	Gas Flow (L/min)	
Beta lactam	Ampicillin	30	3	220	6	
	Ceftriaxone	-	-	-	-	
	Cephalexin	30	5	200	6	
	Penicillin G	150	3	260	6	
Macrolides	Erythromycin	100	5	220	9	
	Tylosin	230	3	200	6	
Sulfonamides	Sulfamethoxazole	50	4	200	6	
	Trimethoprim	100	4	320	10	
Tetracycline	Oxytetracycline	-	-	-	-	
	Tetracycline	30	6	300	6	
Nitroimidazole	Metronidazole	50	3	260	10	
	1,2 dimethyl-5-nitroimidazole	80	3	340	10	

S7: Optimized MS parameters for EDCs precursor ion (APPI)						
Class	Compound	Frag (V)	CAV (V)	Temp (°C)	Gas Flow (L/min)	
Beta blockers	Propranolol	100	8	240	9	
	Metoprolol	65	4	320	10	
	Acebutolol	130	5	200	9	
	Atenolol	100	7	200	11	
Selective serotonin reuptake inhibitor	Venlafaxine	80	3	200	6	
	Citalopram	80	3	220	6	
	Paroxetine	130	3	350	8	

S8: Optimized MS parameters for antibiotics product ion (ESI)

Compound	Precursor Ion (m/z)	Product Ion (m/z)	CE	Product Ion (m/z)	CE	Product Ion (m/z)	CE
Tylosin	916.5	174.0	45	772.3	30	318.1	30
1,2 dimethyl-5-nitroimidazole	142.1	111.9	15	81.8	30	--	-
Ceftriaxone	555.1	166.9	25	124.9	40	--	-
Trimethoprim	291.1	260.9	25	275.0	25	233	35
Metronidazole	172.1	128.0	15	81.4	30	--	-
Penicillin G	335.1	201.9	25	217.0	10	220	10
Erythromycin	734.5	158.1	30	576.1	15	116	50
Oxytetracycline	461.2	426.0	15	444.0	10	--	-
Sulfamethoxazole	254.1	155.8	15	108.0	25	--	-
Tetracycline	445.2	410.0	15	427.0	10	153.9	30
Ampicillin	350.1	106.0	20	159.9	5	333	5
Cephalexin	348.1	158.0	5	106.0	30	174	10

S9: Optimized MS parameters for EDCs product ion (ESI)

Compound	Precursor Ion (m/z)	Product Ion (m/z)	CE
Acebutolol	337.2	319.2	15
		260.1	20
		116.2	20
Atenolol	267.2	145.1	25
		190.1	15
		225.2	15
		107.1	50
Citalopram	325.2	109.0	25
		262.1	15
		247.1	30
		245.1	45
Metoprolol	268.2	116.1	15
		121.0	20
		133.0	25
		103.1	40
		226.1	10
Paroxetine	330.2	192.2	20
		109.1	45
		163.1	25
Propranolol	260.2	116.1	15
		183.1	15
		157.1	20
		127.1	45
Venlafaxine	278.2	260.1	5
		121.0	30
		215.1	15

S10: Optimized MS parameters for antibiotics product ion (APPI)

Compound	Precursor Ion (<i>m/z</i>)	Product Ion (<i>m/z</i>)	CE	Product Ion (<i>m/z</i>)	CE
Tylosin	916.5	174.0	40	772.3	30
Sulfamethoxazole	254.1	155.9	10	107.9	25
Cephalexin	348.1	157.9	5	105.9	25
Ampicillin	350.1	106.0	15	159.9	10
Erythromycin	734.5	158.0	30	576.3	15
Metronidazole	172.1	127.9	15	82.0	30
Penicillin G	335.1	217.0	10	160.0	15
Tetracycline	445.2	410.1	15	427.0	5
Trimethoprim	291.1	122.9	25	260.9	25
1,2 dimethyl-5-nitroimidazole	142.1	111.8	10	-	-

S11: Optimized MS parameters for EDCs product ion (APPI)

Compound	Precursor Ion (<i>m/z</i>)	Product Ion (<i>m/z</i>)	CE
Acebutolol	337.2	116.1	20
		319.2	15
		222.1	20
Atenolol	267.2	145.1	25
		190.2	15
		107.1	45
Citalopram	325.2	109.1	30
		262.0	20
		247.0	35
Metoprolol	268.2	191.0	15
		133.1	25
		121.1	25
		103.1	45
		105.1	35
		226.0	15
Paroxetine	330.2	192.1	20
		190.1	20
		163.1	25
Propranolol	260.2	116.1	15
		183.0	15
		157.1	15
		127.0	45
Venlafaxine	278.2	121.0	35
		215.1	15
		260.9	5

S12: Regression data for antibiotic (ESI)

Antibiotics	ESI				
	Calibration Range	Equation	LOD (ppb)	LOQ (ppb)	R ²
Ampicillin	1 ppt-10 ppm	$y = 0.1195x^2 + 27.282x + 1.2914$	<0.001	<0.001	1.000
Ceftriaxone	1 ppb-10 ppm	$y = -0.0017x^2 + 0.0899x + 0.3388$	<0.001	<0.001	0.9964
Cephalexin	1 ppb-10 ppm	$y = -0.1862x^2 + 8.5956x + 0.6072$	<0.001	<0.001	1.000
Penicillin G	1 ppt-10 ppm	$y = 2.2763x + 0.3339$	45.90	139.1	0.9995
Erythromycin	1 ppt-10 ppm	$y = 8.4663x - 0.3168$	0.3821	1.158	0.9992
Tylosin	1 ppt-1 ppm	$y = -0.6059x^2 + 2.3843x + 0.0352$	<0.001	5.337	0.9990
Sulfamethoxazole	1 ppt-10 ppm	$y = 0.0298x^2 + 4.139x + 0.5791$	<0.001	226.1	1.000
Trimethoprim	1 ppt-10 ppm	$y = 9.5268x + 0.3626$	26.77	81.11	0.9997
Oxytetracycline	1 ppt-10 ppm	$y = 0.213x^2 + 3.497x + 0.8705$	<0.001	<0.001	1.000
Tetracycline	1 ppt-10 ppm	$y = 0.0565x^2 + 1.6314x + 1.3018$	<0.001	<0.001	0.9998
Metronidazole	1ppt-10ppm	$y = -0.1731x^2 + 9.0696x + 1.3726$	<0.001	<0.001	1.000
1,2 dimethyl-5-nitroimidazole	1 ppt-10 ppm	$y = 0.8179x + 1.0161$	55.83	169.2	0.9993

S13: Regression data for EDCs (ESI)

EDCs	ESI				
	Calibration Range	Equation	LOD (ppb)	LOQ (ppb)	R ²
Acebutolol	1 ppt-10 ppm	$y = 113.16x + 11.481$	4.888	14.81	0.9964
Atenolol	1 ppt-1 ppm	$y = 9.1897x + 1.0866$	3.193	9.676	0.9924
Citalopram	1 ppt-100 ppb	$y = 453.65x^2 + 146.27x + 3.9554$	55.48	166.2	0.9992
Metoprolol	1 ppt-1 ppm	$y = 13.492x + 0.8303$	2.869	8.694	0.9971
Paroxetine	1 ppt-3 ppm	$y = -3.6811x^2 + 31.624x + 2.722$	<0.001	<0.001	0.9992
Propranolol	10 ppt-3 ppm	$y = -7.4078x^2 + 62.387x + 0.8008$	<0.001	<0.001	0.9998
Venlafaxine	1 ppt-100 ppb	$y = 126.42x^2 + 855.47x + 5.5899$	<0.001	<0.001	0.9996

S14: Regression data for antibiotic (APPI)

Antibiotics	APPI				
	Calibration Range	Equation	LOD (ppb)	LOQ (ppb)	R ²
Ampicillin	300 ppb-10 ppm	$y = 0.0504x^2 + 0.3264x + 0.9381$	<0.001	<0.001	0.9989
Ceftriaxone	--	--	--	--	--
Cephalexin	300 ppb-10 ppm	$y = 0.0103x^2 + 0.0365x + 0.9926$	<0.001	<0.001	0.9996
Penicillin G	1 ppt-10 ppm	$y = 0.0716x^2 + 0.2646x + 0.9838$	<0.001	<0.001	1.000
Erythromycin	1 ppt-10 ppm	$y = 6.1194x - 0.0005$	53.63	162.5	0.9955
Tylosin	1 ppt-10 ppm	$y = 0.4415x^2 + 0.4788x + 0.9123$	1444	3401	0.9999
Sulfamethoxazole	1 ppt-10 ppm	$y = 8.062x + 0.2749$	23.39	70.87	0.9992
Trimethoprim	1 ppt-10 ppm	$y = 0.0744x^2 + 5.777x + 0.4943$	<0.001	<0.001	1.000
Oxytetracycline	--	--	--	--	--
Tetracycline	1 ppt-10 ppm	$y = 0.0004x^2 + 0.0006x + 0.9998$	<0.001	<0.001	0.9988
Metronidazole	1 ppt-10 ppm	$y = 91.933x + 5.2151$	0.9719	2.945	0.9991
1,2 dimethyl-5-nitroimidazole	1 ppt-10 ppm	$y = 3.2897x + 1.0074$	6.570	19.91	0.9997

S15: Regression data for EDCs (APPI)

EDCs	APPI				
	Calibration Range	Equation	LOD (ppb)	LOQ (ppb)	R ²
Acebutolol	1 ppt-10 ppm	$y = 9.9195x + 2.1595$	12.66	38.37	0.9961
Atenolol	1 ppt-1 ppm	$y = 11.256x + 1.1716$	7.406	22.44	0.9998
Citalopram	1 ppt-10 ppm	$y = -1.0394x^2 + 31.098x + 1.1429$	<0.001	<0.001	0.9999
Metoprolol	1 ppt-10 ppm	$y = 4.2856x + 1.1597$	7.147	21.66	0.9988
Paroxetine	100 ppt-1 ppm	$y = 0.2372x^2 + 0.0208x + 0.956$	<0.001	<0.001	0.9907
Propranolol	10 ppt-10 ppm	$y = -0.021x^2 + 7.3169x + 1.0553$	<0.001	<0.001	1.000
Venlafaxine	1 ppt-10 ppm	$y = 0.257x + 0.9367$	1250	3788	0.9985

S16: P-value for sample means performed on antibiotics

Antibiotics	P-value	
	ESI	APPI
Trimethoprim	0.0411*	0.332
Ampicillin	0.402	0.250
Ceftriaxone	0.0000610*	-
Cephalexin	0.908	0.276
Erythromycin	0.023*	0.366
Oxytetracycline	0.285	-
Penicillin G	0.038*	0.357
Sulfamethoxazole	0.175	0.242
Tetracycline	0.304	0.934
Tylosin	0.310	0.360
Metronidazole	0.141	0.393
1,2 dimethyl-5-nitroimidazole	0.0778	0.391

S17: P value for sample means performed on EDCs

EDCs	P-value	
	ESI	APPI
Acebutolol	0.288	0.526
Atenolol	0.377	0.312
Citalopram	0.0539	0.261
Metoprolol	0.0690	0.504
Paroxetine	0.045*	0.300
Propranolol	0.0634	0.344
Venlafaxine	0.399	0.114

S18: P-value antibiotics concentration on real wastewater sample

Antibiotics	P-value	
	With Matrix	Without Matrix
Trimethoprim	0.642	0.765
Ampicillin	--	--
Ceftriaxone	--	--
Cephalexin	0.0140	0.0265
Erythromycin	0.0823	0.0824
Oxytetracycline	--	--
Penicillin G	0.0115	0.253
Sulfamethoxazole	0.0152	0.00908
Tetracycline	--	--
Tylosin	0.144	--
Metronidazole	0.218	--
1,2 dimethyl-5-nitroimidazole	--	--

S19: P-value EDCs concentration performed on real wastewater sample

EDCs	P-value	
	With Matrix	Without Matrix
Acebutolol	0.113	0.110
Atenolol	--	--
Citalopram	--	0.0464
Metoprolol	--	--
Paroxetine	--	0.112
Propranolol	0.0273	0.0862
Venlafaxine	0.0179	0.0159

S20: Table of calibration parameters for all compounds with and without matrix (nd = not detected).

Compound	Class	Ionization	Matrix	Regression Type	Coefficient of Determination	a	b	c
1,2-Dimethyl-5-nitroimidazole	Antibiotic	APPI	-	Linear	0.9997	-	3.2897	1.0074
1,2-Dimethyl-5-nitroimidazole	Antibiotic	APPI	+	Linear	0.9972	-	12.459	1.0366
Ampicillin	Antibiotic	APPI	-	Quadratic	0.9989	0.0504	0.3264	0.9381
Ampicillin	Antibiotic	APPI	+	Quadratic	0.9995	0.0295	-0.0629	1.0107
Ceftriaxone	Antibiotic	APPI	-	nd	nd	nd	nd	nd
Ceftriaxone	Antibiotic	APPI	+	nd	nd	nd	nd	nd
Cephalexin	Antibiotic	APPI	-	Quadratic	0.9996	0.0103	0.0365	0.9926
Cephalexin	Antibiotic	APPI	+	Quadratic	0.9994	0.0029	-0.0045	1.0013
Erythromycin	Antibiotic	APPI	-	Linear	0.9955	-	6.1194	-0.0005
Erythromycin	Antibiotic	APPI	+	Linear	0.9923	-	1.9959	0.7246
Metronidazole	Antibiotic	APPI	-	Linear	0.9991	-	91.933	5.2151
Metronidazole	Antibiotic	APPI	+	Linear	0.9972	-	320.32	1.6072
Oxytetracycline	Antibiotic	APPI	-	nd	nd	nd	nd	nd
Oxytetracycline	Antibiotic	APPI	+	nd	nd	nd	nd	nd
Penicillin G	Antibiotic	APPI	-	Quadratic	1	0.0716	0.2646	0.9838
Penicillin G	Antibiotic	APPI	+	Quadratic	0.9985	0.0234	-0.0481	1.0186
Sulfamethoxazole	Antibiotic	APPI	-	Linear	0.9992	-	8.062	0.2749
Sulfamethoxazole	Antibiotic	APPI	+	Linear	0.9989	-	20.673	4.1751
Tetracycline	Antibiotic	APPI	-	Quadratic	0.9988	0.0004	0.0006	0.9998
Tetracycline	Antibiotic	APPI	+	Quadratic	0.9902	0.0004	0.0061	0.9818
Trimethoprim	Antibiotic	APPI	-	Quadratic	1.0000	0.0744	5.7770	0.4943
Trimethoprim	Antibiotic	APPI	+	Quadratic	0.9995	-7.2209	48.567	-0.0299
Tylosin	Antibiotic	APPI	-	Quadratic	0.9999	0.4415	0.4788	0.9123
Tylosin	Antibiotic	APPI	+	Quadratic	0.9998	1.3127	5.9593	-0.0348
1,2-Dimethyl-5-nitroimidazole	Antibiotic	ESI	-	Linear	0.9993	-	0.8179	1.0161
1,2-Dimethyl-5-nitroimidazole	Antibiotic	ESI	+	Linear	0.9993	-	1.1605	1.0281
Ampicillin	Antibiotic	ESI	-	Quadratic	1.0000	0.1195	27.282	1.2914
Ampicillin	Antibiotic	ESI	+	Quadratic	0.9843	-1.8902	11.1100	0.1452

S20: Table of calibration parameters for all compounds with and without matrix (nd = not detected). [continued]

Compound	Class	Ionization	Matrix	Regression Type	Coefficient of Determination	a	b	c
Ceftriaxone	Antibiotic	ESI	-	Quadratic	0.9964	-0.0017	0.0899	0.3388
Ceftriaxone	Antibiotic	ESI	+	Quadratic	0.9925	-0.0049	0.0417	0.9717
Cephalexin	Antibiotic	ESI	-	Quadratic	1.0000	-0.1862	8.5956	0.6072
Cephalexin	Antibiotic	ESI	+	Quadratic	0.9876	-1.5218	9.3825	0.0565
Erythromycin	Antibiotic	ESI	-	Linear	0.9992	-	8.4663	-0.3168
Erythromycin	Antibiotic	ESI	+	Linear	0.9976	-	6.6874	-0.0191
Metronidazole	Antibiotic	ESI	-	Quadratic	1.0000	-0.1731	9.0696	1.3726
Metronidazole	Antibiotic	ESI	+	Quadratic	1.0000	4.064	4.6606	1.2965
Oxytetracycline	Antibiotic	ESI	-	Quadratic	1.0000	0.2130	3.4970	0.8705
Oxytetracycline	Antibiotic	ESI	+	Quadratic	0.9994	-3.7032	31.2120	1.7656
Penicillin G	Antibiotic	ESI	-	Linear	0.9995	-	2.2763	0.3339
Penicillin G	Antibiotic	ESI	+	Linear	0.9976	-	3.9488	0.9507
Sulfamethoxazole	Antibiotic	ESI	-	Quadratic	1.0000	0.0298	4.1390	0.5791
Sulfamethoxazole	Antibiotic	ESI	+	Quadratic	0.9986	-0.4447	12.1310	3.9652
Tetracycline	Antibiotic	ESI	-	Quadratic	0.9998	0.0565	1.6314	1.3018
Tetracycline	Antibiotic	ESI	+	Quadratic	0.9990	-2.0844	18.4740	1.4178
Trimethoprim	Antibiotic	ESI	-	Linear	0.9997	-	9.5268	0.3626
Trimethoprim	Antibiotic	ESI	+	Quadratic	0.9996	30.052	32.2360	3.2322
Tylosin	Antibiotic	ESI	-	Quadratic	0.9999	-0.6059	2.3843	0.0352
Tylosin	Antibiotic	ESI	+	Quadratic	0.9982	-0.8132	19.4230	0.3437
Acebutolol	EDC	APPI	-	Linear	0.9961	-	9.9195	2.1595
Acebutolol	EDC	APPI	+	Linear	0.9925	-	3.3775	1.9337
Atenolol	EDC	APPI	-	Linear	0.9998	-	11.256	1.1716
Atenolol	EDC	APPI	+	Linear	0.9963	-	1.4015	0.9857
Citalopram	EDC	APPI	-	Quadratic	0.9999	-1.0394	31.098	1.1429
Citalopram	EDC	APPI	+	Linear	0.9902	-	25.224	7.8397
Metoprolol	EDC	APPI	-	Linear	0.9988	-	4.2856	1.1597
Metoprolol	EDC	APPI	+	Linear	0.9993	-	5.3085	1.0077
Paroxetine	EDC	APPI	-	Quadratic	0.9907	0.2372	0.0208	0.956
Paroxetine	EDC	APPI	+	Quadratic	0.992	-0.3002	1.8603	0.9305
Propranolol	EDC	APPI	-	Quadratic	1	-0.021	7.3169	1.0553
Propranolol	EDC	APPI	+	Quadratic	0.9997	7.5587	12.386	1.1305

S20: Table of calibration parameters for all compounds with and without matrix (nd = not detected). [continued]

Compound	Class	Ionization	Matrix	Regression Type	Coefficient of Determination	a	b	c
Venlafaxine	EDC	APPI	-	Linear	0.9985	-	0.257	0.9367
Venlafaxine	EDC	APPI	+	Linear	0.9949	-	0.404	0.9637
Acebutolol	EDC	ESI	-	Linear	0.9964	-	113.1600	11.481
Acebutolol	EDC	ESI	+	Linear	0.9970	-	54.3550	2.6236
Atenolol	EDC	ESI	-	Linear	0.9924	-	9.1897	1.0866
Atenolol	EDC	ESI	+	Linear	0.9948	-	2.3403	0.9909
Citalopram	EDC	ESI	-	Quadratic	0.9992	453.65	146.2700	3.9554
Citalopram	EDC	ESI	+	Quadratic	0.9816	-2.5202	63.1280	139.5
Metoprolol	EDC	ESI	-	Linear	0.9971	-	13.4920	0.8303
Metoprolol	EDC	ESI	+	Linear	0.9989	-	16.8600	1.6913
Paroxetine	EDC	ESI	-	Quadratic	0.9992	-3.6811	31.6240	2.722
Paroxetine	EDC	ESI	+	Quadratic	0.9920	-1.7436	46.0100	15.254
Propranolol	EDC	ESI	-	Quadratic	0.9998	-7.4078	62.3870	0.8008
Propranolol	EDC	ESI	+	Quadratic	0.9981	-47.902	124.2400	3.13
Venlafaxine	EDC	ESI	-	Quadratic	0.9996	126.42	855.4700	5.5899
Venlafaxine	EDC	ESI	+	Quadratic	0.9916	-134.81	348.7900	11.683