Identifying Unknown Chemicals and Disinfection Byproducts in Swimming Pools and Hot Tubs

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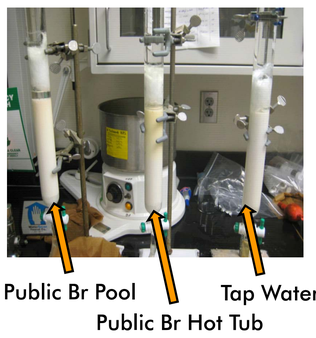
Introduction

- Swimming pools are treated with disinfectants to protect swimmers from pathogens and prevent illness.
- Disinfectants will react with naturally occurring organic matter in water and, in the case of swimming pools, they can also react with chemicals introduced to the water by the swimmers themselves to produce byproducts that can be potentially harmful.
- It is important to treat water while minimizing the risk of disinfection byproducts (DBPs).
- One of the first steps is to chemically characterize the DBPs in swimming pools and hot tubs (very complex matrices), using non-targeted analysis since many of the contaminants are unknowns.
- Gas chromatography with high resolution time-of-flight mass spectrometry (GC-HRT) was used for the identification of "known unknowns" and "unknown unknowns" in swimming pool and hot tub water.

Methods

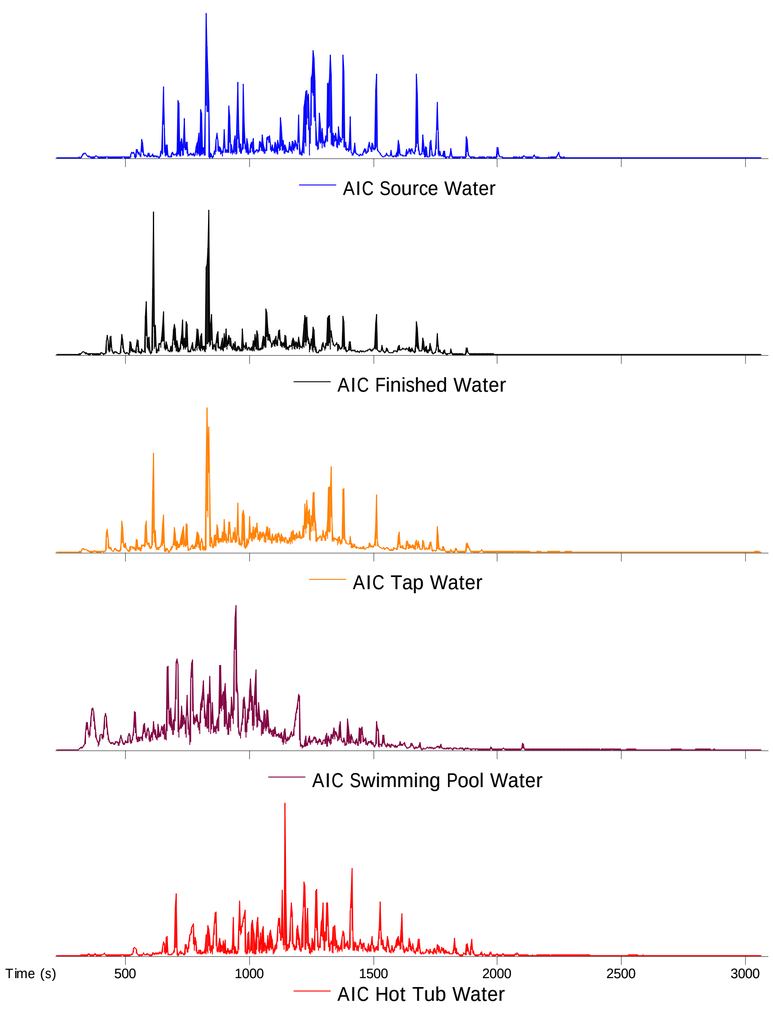
Sample Preparation

- Collected water for two complete water pathways Source » Finished » Tap » Pool or Spa
- Amberlite XAD resin extraction (10 L), concentrate to 1 mL
- Derivatize ½ mL with diazomethane (halo-acids)

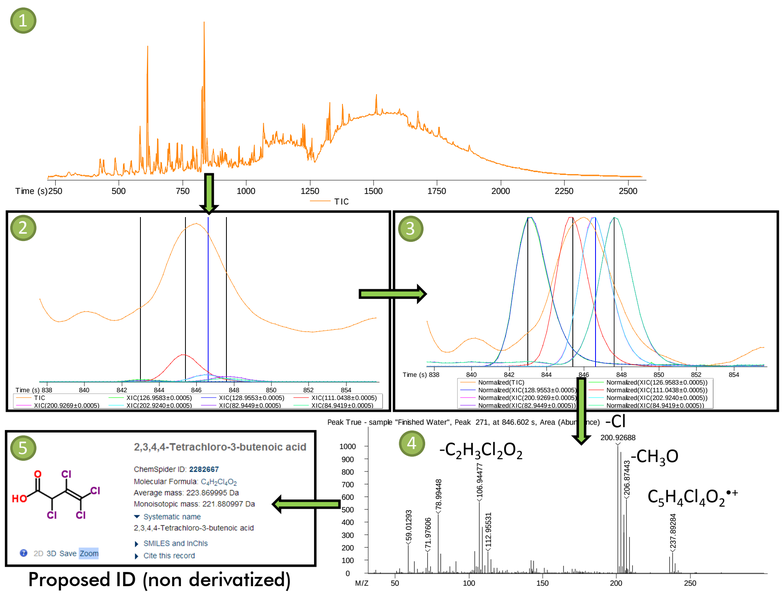


Instrumental Analysis

- 25,000 mass resolution
- m/z range from 33 to 650
- 5 spectra/s
- ChromaTOF-HRT® data processing



The analytical ion chromatograms (AIC) above, showing base peak intensity for deconvoluted peaks, illustrate the complexity of the samples.



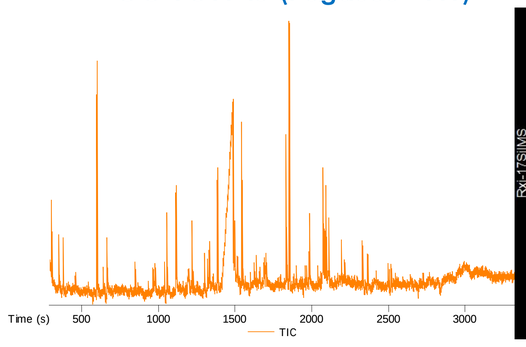
Proposed ID (non derivatized)

(1) Total ion chromatogram (TIC) of the finished water sample; (2) Zoomed-in view of the TIC showing four deconvoluted peaks under one peak in the TIC; (3) Normalized view of the zoomed-in region showing XICs of the deconvoluted masses with the TIC; (4) Mass spectrum of the peak marker highlighted in blue; (5) Proposed ID.

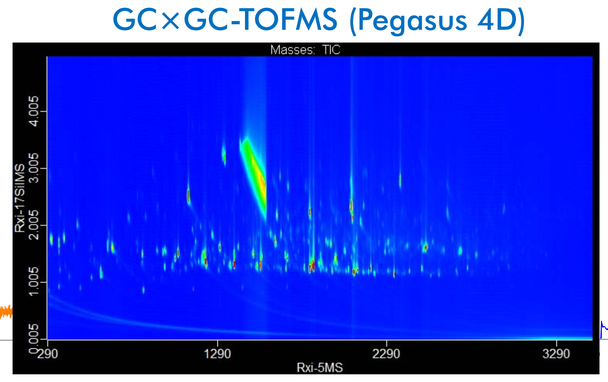
Results

These complex samples require high resolution, accurate mass data with High Resolution Deconvolution™ because of chromatographic coelutions and lack of mass spectral library databases for the majority of the non-target analytes.

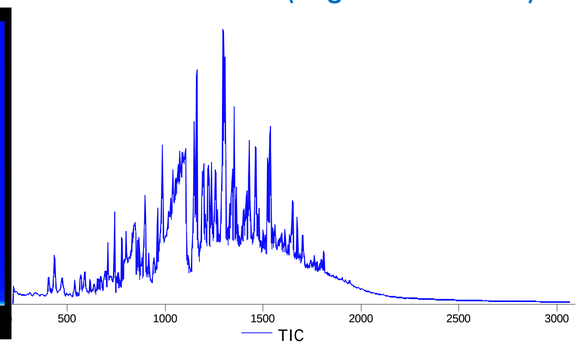
GC-TOFMS (Pegasus® HT)



GC×GC-TOFMS (Pegasus 4D)

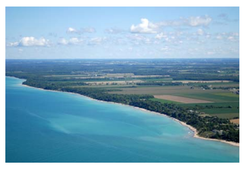


GC-HR-TOFMS (Pegasus GC-HRT)



Comparison of halogenated species in the water cycle from source-to-swimming pool, and source-to-hot tub considering identifications with a library similarity >800 (out of 1000) **Known–Unknowns.**

Source Water



Name	Formula	R.T. (s)	Similarity	Peak S/N
Acetic acid, trichloro-, methyl ester	C3H3Cl3O2	425.0	877	104
2,3,4,5,6-Pentafluorobenzyl alcohol	C7H3F5O	553.6	857	153
Acetone, (O-pentafluorobenzyl)oxime	C10H8F5NO	735.4	876	186
Hydroxylamine, O-[(pentafluorophenyl)methyl]-	C7H4F5NO	1056.4	830	249
Trichloroacetic acid, pentafluorobenzyl ester	C9H2Cl3F5O2	1125.2	845	541
1,2-Benzenediol, o-(4-methoxybenzoyl)-o'-(2,2,3,3,4,4,4-heptafluorobutyryl)-	C18H11F7O5	1234.6	901	630
Tris(1-chloro-2-propyl)phosphate	C9H18Cl3O4P	1293.6	842	199

Finished Water

Name	Formula	R.T. (s)	Similarity	Peak S/N
2-Bromo-2-nitropropane	C3H6BrNO2	317.4	890	112
Acetic acid, dichloro-, methyl ester	C3H4Cl2O2	323.2	855	73
Methane, tribromo-	CHBr3	365.6	829	87
Acetonitrile, dibromo-	C2HBr2N	416.0	901	85
Acetic acid, trichloro-, methyl ester	C3H3Cl3O2	426.2	952	664
1-Bromo-1,1-dichloro-2-propanone	C3H3BrCl2O	446.8	808	159
Acetic acid, dibromo-, methyl ester	C3H4Br2O2	535.8	852	114
Methyl bromodichloroacetate	C3H3BrCl2O2	548.4	905	315
2-Propanone, 1,1,3,3-tetrachloro-	C3H2Cl4O	584.0	919	449
2-Propanone, 1,1,1,3-tetrachloro-	C3H2Cl4O	592.6	881	277
Acetamide, 2,2,2-trichloro-	C2H2Cl3NO	729.6	920	740
Phenol, 2,4-dichloro-	C6H4Cl2O	737.6	936	295
Methane, dichloronitro-	CHCl2NO2	889.6	837	407
Phenol, 2,3,6-trichloro-	C6H3Cl3O	922.2	860	192
(E)-2-Chloro-3-(dichloromethyl)-butenedioic acid dimethyl ester (methyla ted ox-emx)	C7H7Cl3O4	1031.2	843	192
1,4-Benzenediol, 2,5-dichloro-	C6H4Cl2O2	1119.4	853	402
Acetic acid, (2,4-dichlorophenoxy)-, methyl ester	C9H8Cl2O3	1167.8	830	109
1,2-Benzenediol, o-(4-methoxybenzoyl)-o'-(2,2,3,3,4,4,4-heptafluorobutyryl)-	C18H11F7O5	1244.4	867	325

Tap Water

Name	Formula	R.T. (s)	Similarity	Peak S/N
Acetic acid, dichloro-, methyl ester	C3H4Cl2O2	324.6	866	71
Propanoic acid, 2,2-dichloro-, methyl ester	C4H6Cl2O2	342.8	890	182
2-Propanone, 1,3-dichloro-	C3H4Cl2O	383.0	852	155
Oxirane, (trichloromethyl)-	C3H3Cl3O	407.6	847	83
Acetic acid, trichloro-, methyl ester	C3H3Cl3O2	425.8	946	808
Propane, 1,2-epoxy-2-methyl-3,3,3-trichloro-	C4H5Cl3O	499.0	893	211
Acetamide, 2,2,2-trichloro-	C2H2Cl3NO	732.2	912	653
Benzene, 2,4-dichloro-1-methoxy-	C7H6Cl2O	860.2	912	251
Methane, dichloronitro-	CHCl2NO2	890.2	890	451
Benzene, 1,3,5-trichloro-2-methoxy-	C7H5Cl3O	898.6	947	259
Chloroneb	C8H8Cl2O2	1000.6	885	501
(E)-2-Chloro-3-(dichloromethyl)-butenedioic acid dimethyl ester (methyla ted ox-emx)	C7H7Cl3O4	1031.4	847	292
Tris(1-chloro-2-propyl)phosphate	C9H18Cl3O4P	1295.8	863	239

Swimming Pool Water

Name	Formula	R.T. (s)	Similarity	Peak S/N
Methane, tribromo-	CHBr3	367.2	984	2391
Acetonitrile, dibromo-	C2HBr2N	419.2	937	1575
Acetic acid, trichloro-, methyl ester	C3H3Cl3O2	428.0	936	885
Ethene, tribromo-	C2HBr3	499.4	823	297
Acetic acid, dibromo-, methyl ester	C3H4Br2O2	537.6	934	1147
Chlorodibromoacetic acid, methyl ester	C3H3Br2ClO2	660.4	881	290
2-Propenoic acid, 3,3-dibromo-, methyl ester	C4H4Br2O2	681.2	826	850
2-Butenedicarbonic acid,-2-bromo, dimethyl ester	C6H7BrO4	778.6	818	538
2-Butenedicarbonic acid,-2-bromo, dimethyl ester	C6H7BrO4	850.8	842	660
Phenol, 4-bromo-	C6H5BrO	881.2	803	272
Benzoic acid, 4-bromo-, methyl ester	C8H7BrO2	921.2	824	452
Phenol, 2,4-dibromo-	C6H4Br2O	925.6	855	487
Benzoic acid, 2,4-dichloro-, methyl ester	C8H6Cl2O2	976.4	895	520
Benzene, 1,2,4-tribromo-	C6H3Br3	987.6	927	289
Phenol, 2,6-dibromo-4-methyl-	C7H6Br2O	1050.2	823	384
Carbon tetrabromide	CBr4	1062.2	810	586
Methyl 3,5-dibromobenzoate	C8H6Br2O2	1127.8	857	286
4-Bromophenoxyacetic acid, methyl ester	C9H9BrO3	1128.8	852	212
2,6-Dibromo-4-chloroaniline	C6H4Br2ClN	1145.2	854	144
Benzene, 1,3,5-tribromo-2-methoxy-	C7H5Br3O	1154.4	820	171
Phenol, 2,4,6-tribromo-	C6H3Br3O	1177.2	939	414
Benzoic acid, 3-bromo-4-methoxy-, methyl ester	C9H9BrO3	1191.8	870	305
Benzenamine, 2,4,6-tribromo-	C6H4Br3N	1226.2	925	455
1-(2,3,4,5,6-Pentachlorobenzoyl)pyrrole	C11H4Cl5NO	1340.0	832	265
2,3,5,6-Tetrachloro-1,4-benzenedicarboxilic acid dimethyl ester	C10H6Cl4O4	1454.4	825	379

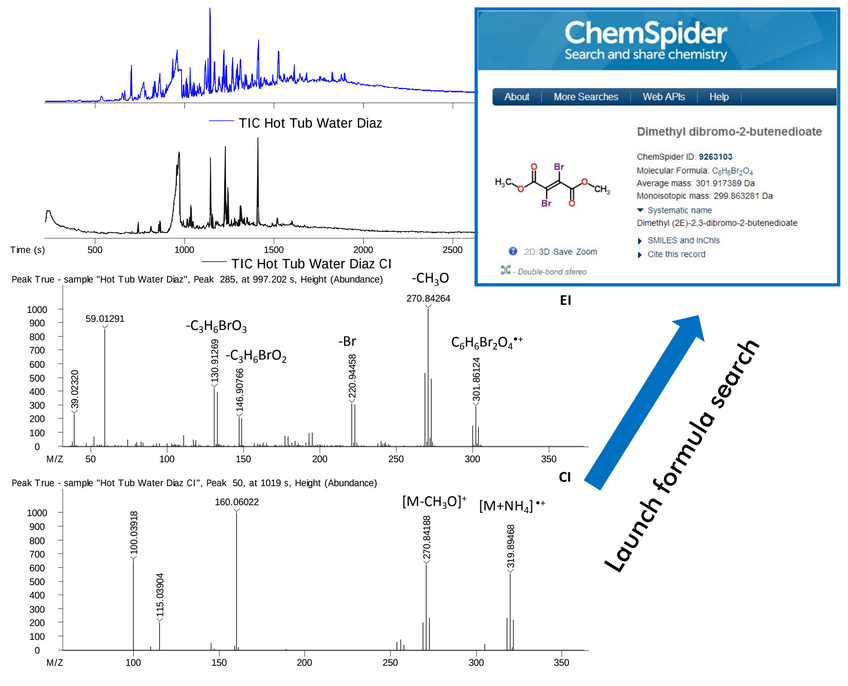
Hot Tub Water

Name	Formula	R.T. (s)	Similarity	Peak S/N
Methane, tribromo-	CHBr3	377.0	970	111
Acetonitrile, dibromo-	C2HBr2N	414.2	933	192
Ethene, tribromo-	C2HBr3	496.8	812	40
Acetic acid, dibromo-, methyl ester	C3H4Br2O2	535.2	917	218
Bromomaleic anhydride	C4HBrO3	572.6	913	105
2-Propenoic acid, 3,3-dibromo-, methyl ester	C4H4Br2O2	679.8	886	67
Dibromomaleic anhydride	C4Br2O3	755.6	837	108
Tribromoacetic acid, methyl ester	C3H3Br3O2	762.4	913	84
1,1,3-Tribromoacetone	C3H3Br3O	788.6	827	74
2-Butenedicarbonic acid,-2-bromo, dimethyl ester	C6H7BrO4	847.4	898	151
Phenol, 2,6-dibromo-	C6H4Br2O	915.4	821	56
1,1,3,3-Tetrabromoacetone	C3H2Br4O	975.6	871	74
Benzene, 1,2,4-tribromo-	C6H3Br3	985.4	951	77
Phenol, 2,6-dibromo-4-methyl-	C7H6Br2O	994.6	824	112
Imidazole, 2,4,5-tribromo-1-methyl-	C4H3Br3N2	1045.0	895	219
Methyl 3,5-dibromobenzoate	C8H6Br2O2	1128.0	819	133
Benzene, 1,3,5-tribromo-2-methoxy-	C7H5Br3O	1132.6	819	45
Phenol, 2,4,6-tribromo-	C6H3Br3O	1151.6	884	115
Benzenamine, 2,4,6-tribromo-	C6H4Br3N	1170.0	954	287
1,2-Benzenediol, o-(4-methoxybenzoyl)-o'-(2,2,3,3,4,4,4-heptafluorobutyryl)-	C18H11F7O5	1221.6	921	425
1,3-Dibromo-2-methoxy-5-nitrobenzene	C7H5Br2NO3	1224.2	858	161
2,6-Dibromohydroquinone	C6H4Br2O2	1247.2	832	100
Tris(1-chloro-2-propyl)phosphate	C9H18Cl3O4P	1272.2	884	286
Methyl 2-amino-3,5-dibromobenzoate	C8H7Br2NO2	1298.0	820	83
Benzenamine, 2,6-dibromo-4-nitro-	C6H4Br2N2O2	1305.6	883	193
Phthalic acid, 4-fluoro-2-nitrophenyl methyl ester	C15H10FNO6	1384.8	904	103
		2020.2	867	50

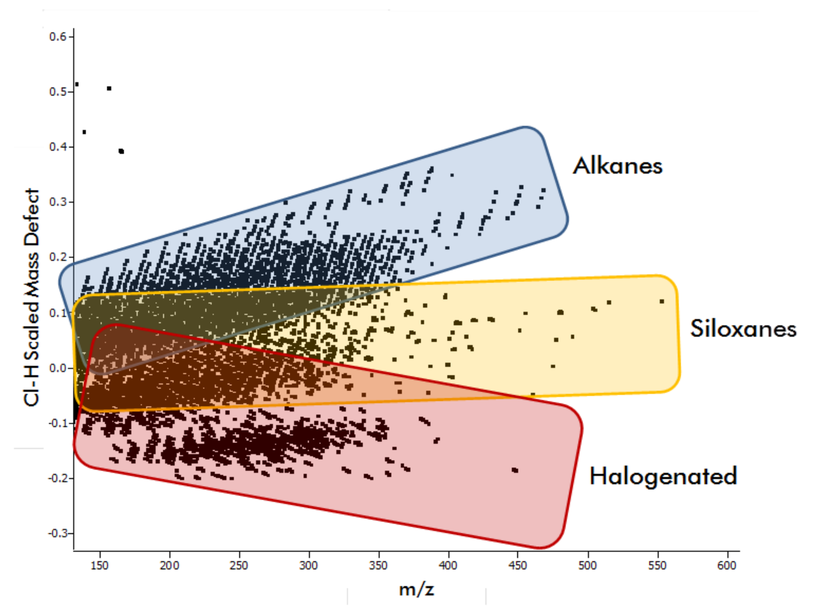
Table Legend

- brominated species
- chlorinated species
- mixed bromo/chloro species

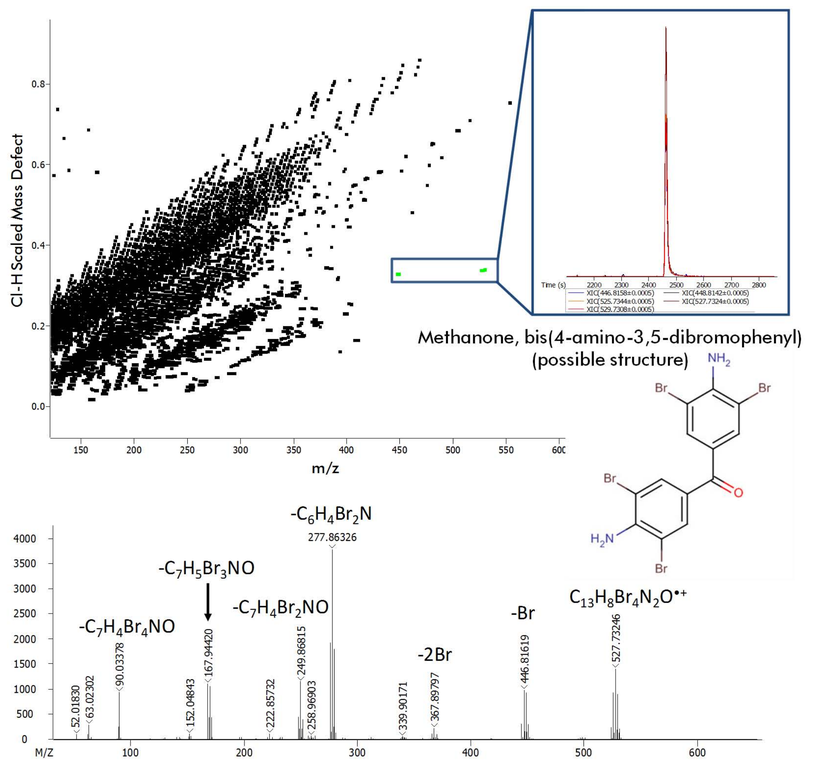
Unknown identification using complementary EI and CI data



Mass defect plot of the swimming pool sample highlights regions to search for **Unknown-Unknowns**.



Utilization of Cl-H mass defect plot for the isolation of brominated/chlorinated species in the swimming pool sample.



The above mass spectrum is for the peak highlighted in the Cl-H mass defect plot and corresponding extracted ion chromatgrams (XICs). The table below shows accurate mass data (most <1 ppm) for the molecular ion and fragment ions.

Formula	Loss	Observed Ion m/z	Expected Ion m/z	Mass Delta (mDa)	Mass Accuracy (ppm)	RDBE
$C_{13}H_8Br_2{}^{81}Br_2N_2O$		527.7325	527.7324	0.088	0.168	9
$C_{13}H_8Br_2{}^{81}BrN_2O$	Br	446.8162	446.8161	0.11	0.246	9.5
$C_{13}H_8Br^{81}BrN_2O$	2Br	367.8980	367.8977	0.224	0.609	10
$C_7H_4Br^{81}BrNO$	$C_6H_4Br_2N$	277.8633	277.8634	-0.107	-0.386	5.5
$C_6H_4Br^{81}BrN$	$C_7H_4Br_2NO$	249.8682	249.8685	-0.307	-1.23	4.5
C_6H_3BrN	$C_7H_5Br_3NO$	167.9442	167.9443	-0.14	-0.835	5.5
C_6H_4N	$C_7H_4Br_4NO$	90.0338	90.0338	-0.044	-0.484	5.5

Conclusions

- DBPs were identified in finished water, tap water, swimming pool water, and hot tub water that were not present in the source water.
- High Resolution Deconvolution was used effectively to identify a greater number of peaks in the chromatogram than by nominal resolution MS.
- Library database searching was used to identify known-unknowns in the water cycle.
- EI and CI accurate mass data were used to tentatively identify unknowns-unknowns with mass accuracy values typically less than 1 ppm.
- Cl-H mass defect plots are a useful tool for isolating unknowns in complex matrices.

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