The Use of Accurate Mass Peak Filters to Detect and Identify New Disinfection Byproducts in Swimming Pools and Spas

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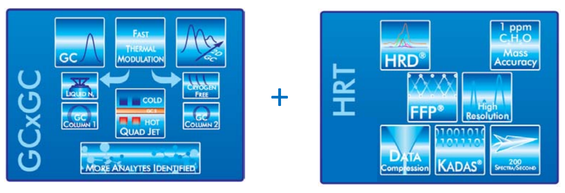
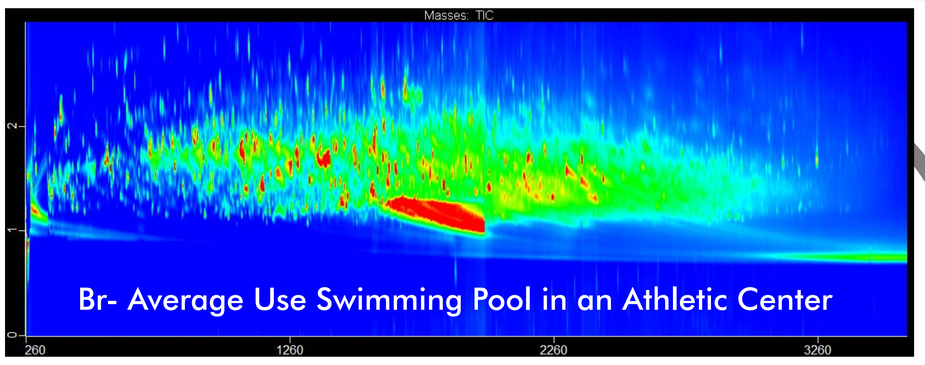
Sample Workflow



Data Acquisition

Collect electron ionization (EI) or chemical ionization (CI) data in high resolution (Resolving Power = 25K FWHH) or ultra high resolution (RP = 50K FWHH) mode at an acquisition rate of up to 200 spectra/second. Combines LECO's market-leading GC×GC technology with high resolution time-of-flight mass spectrometry, all in one integrated platform and software package.

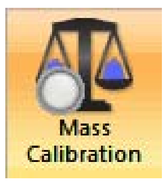


Analytical Conditions:

Primary Column: 30 m x 0.25 mm x 0.25 µm film (Rtx-200)
Sec. Column: 0.6 m x 0.25 mm ID x 0.25 µm film (Rxi-5ms)
Sample: 1 µL cold splitless 250°C
Column Flow: 1.0 mL/min
Injection Temp: 55°C --(300°C/min) - 250°C
Oven Temp: 35°C (4.0 min)--(5°C/min)
-300°C (3.0 min), Total: 60 min
Secondary Oven: +5°C
Modulator: +15°C **Modulation Period**: 3 s
MS Transfer Line Temp: 280°C
Mass Range: m/z 15 – 650
Acquisition Rate: 150 spectra/s
Source Temp: 200°C

Mass Calibration

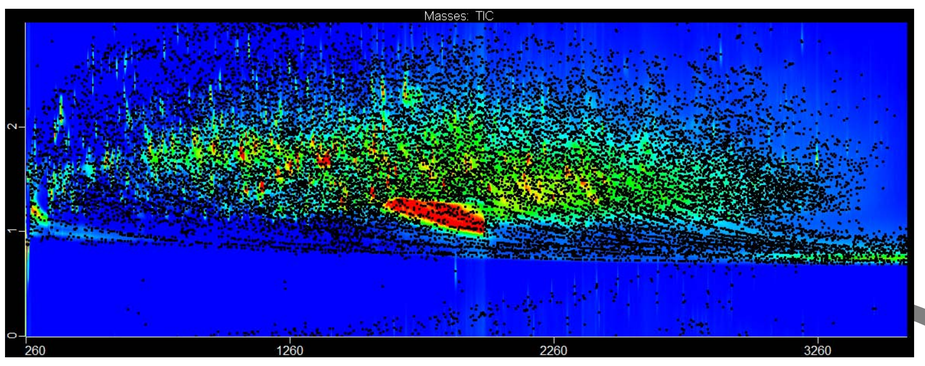
A reference compound such as perfluorotributylamine may be introduced throughout the chromatographic run to enhance the mass accuracy with post-acquisition mass calibration. If the TOF drift correction is stable throughout the run, then a region without analyte interference, such as during the hold time at the end of the run, may be used for post-acquisition mass calibration. The mass calibration table demonstrates a mass accuracy RMS = 0.47 ppm.

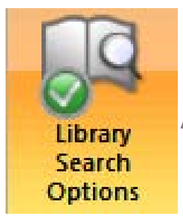


	Name	Formula	Species	Charge	Mass Windo	Start Time (s)	End Time (s)	Priority	Expected M/Z	Observed M/Z	Mass Delta (mDa)	Mass Accuracy (ppm)	Resolution
1*	Carbon dioxide	CO_2		1	0.5000	3396	3510	1	43.9893	43.9893	0.05	1.03	18055
2	PFTBA069	CF_3		1	1.0000	3396	3510	1	68.9947	68.9946	-0.02	-0.32	23900
3	PFTBA131	C_3F_5		1	1.0000	3396	3510	1	130.9915	130.9914	-0.04	-0.32	24619
4	PFTBA219	C_4F_9		1	1.0000	3396	3510	1	218.9851	218.9851	0.02	0.09	25964
5	PFTBA264	$C_5F_{10}N$		1	2.0000	3396	3510	1	263.9866	263.9867	0.12	0.47	24492
6	PFTBA414	$C_8F_{16}N$		1	2.0000	3396	3510	1	413.9770	413.9769	-0.06	-0.14	21318
7	PFTBA502	$C_9F_{20}N$		1	2.0000	3396	3510	1	501.9706	501.9705	-0.11	-0.23	21311

Automatic Peak Finding with Mass Spectral HRD®

Industry leading High Resolution Deconvolution® (HRD) identifies chromatographic peaks automatically. In this swimming pool treated with bromine as the disinfectant, more than 10,000 individual chromatographic peaks were indicated; more than 10x the number of peaks detected in the 1D chromatogram. About 3% of the peaks had a library similarity score greater than 850 and a mass accuracy ±2 ppm, indicating that the large majority of the peaks in the sample were unknowns.



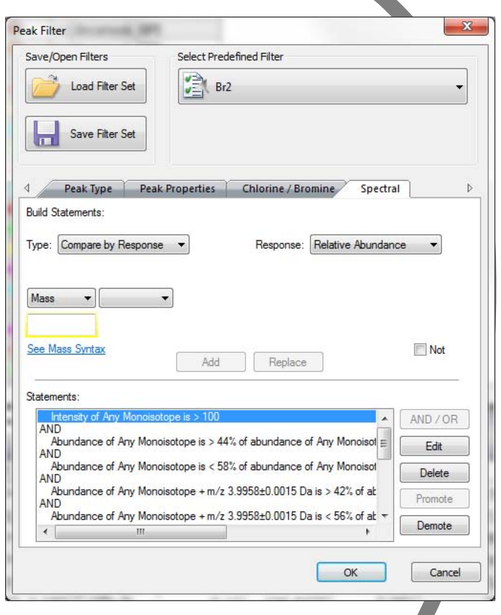


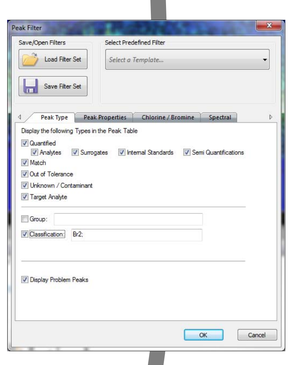
Accurate Mass Peak Filters

A compound class(es) may be identified by leveraging unique features in its mass spectrum; e.g. accurate mass, isotope pattern, and/or fragmentation pattern. Spectral peak filters were designed for Br_x, Cl_y, Br_xCl_y, and I containing compounds; where x = 1 to 5 and y = 1 to 7. The I^+ ion was targeted using m/z 126.9039 ± 5 ppm.

Spectral Peak Filter for Br_2 compound:

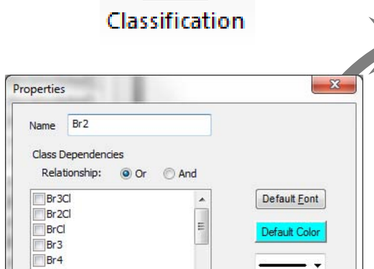
Intensity of Any Monoisotope is > 100
AND
Abundance of Any Monoisotope is > 44% of abundance of Any Monoisotope ± m/z 1.9979±0.0015Da
AND
Abundance of Any Monoisotope is < 58% of abundance of Any Monoisotope ± m/z 1.9979±0.0015Da
AND
Abundance of Any Monoisotope ± m/z 3.9985±0.0015Da is > 42% of abundance of Any Monoisotope ± m/z 1.9979±0.0015Da
AND
Abundance of Any Monoisotope ± m/z 3.9985±0.0015Da is < 56% of abundance of Any Monoisotope ± m/z 1.9979±0.0015Da
AND
Abundance of Any Monoisotope ± m/z 1.0028±0.0015Da is < abundance of Any Monoisotope
AND
Abundance of Any Monoisotope ± m/z 5.9937±0.0015Da is < 2% of abundance of Any Monoisotope ± m/z 1.9979±0.0015Da
AND
Intensity of Any Monoisotope + Br±0.0015Da is < 20
AND
Intensity of Any Monoisotope + Br2±0.0015Da is < 20
AND
Intensity of Any Monoisotope + Cl±0.0015Da is < 20
AND
Intensity of Any Monoisotope + Cl2±0.0015Da is < 20





Classification Table

Create a classification table for the compound class(es) that the spectral peak filters were designed to identify, inserting the appropriate filter into the properties option for the class. One or more summary columns may be added for each class. i.e. XIC, BPI, or TIC. In this case, the summary will be based on the total area of all of the ions in the deconvoluted (peak true) spectra for all of the chromatographic peaks of each class.



#	Show	Class	Component	Region	Color	dTIC
1	☒	Br3Cl				tic(deconvoluted)
2	☒	Br2Cl				tic(deconvoluted)
3	☒	BrCl				tic(deconvoluted)
4	☒	Br3				tic(deconvoluted)
5	☒	Br4				tic(deconvoluted)
6	☒	Br6				tic(deconvoluted)
7	☒	Br2				tic(deconvoluted)
8	☒	Br5				tic(deconvoluted)
9	☒	Cl				tic(deconvoluted)
10	☒	Cl2				tic(deconvoluted)
11	☒	Cl3				tic(deconvoluted)
12	☒	Cl4				tic(deconvoluted)
13	☒	Cl5				tic(deconvoluted)
14	☒	Cl6				tic(deconvoluted)
15	☒	Cl7				tic(deconvoluted)
16	☒	I				tic(deconvoluted)
17	☒	Br				tic(deconvoluted)
18	☒	Br2Cl2				tic(deconvoluted)
19	☒	Br2Cl3				tic(deconvoluted)
20	☒	Br2Cl4				tic(deconvoluted)
21	☒	Br3Cl2				tic(deconvoluted)
22	☒	Br3Cl3				tic(deconvoluted)
23	☒	Br4Cl2				tic(deconvoluted)
24	☒	BrCl2				tic(deconvoluted)
25	☒	BrCl3				tic(deconvoluted)
26*	☒	BrCl4				tic(deconvoluted)
27		Unclassified				tic(deconvoluted)
28	☒	Unassigned				

Unknown Identification

A putative identification can be made for an unknown compound based on the mass spectral interpretation of accurate mass data. After the elemental composition of the molecular ion was determined below, ChemSpider was launched directly from ChromTOF-HRT® brand software to search for compounds matching the chemical formula assigned. Of the 16 results in the database, only two compounds had an appropriate structure that corresponded with the observed mass spectrum. Note that they are positional isomers.

ChemSpider
Search and share chemistry

Found 16 results

Search term: **C8H4Br2N2O2** (Found by molecular formula)

ID	Structure	Molecular Formula	Molecular Weight	# of Data Sources	# of References	# of PubMed	# of RSC
13789183		$C_8H_4Br_2N_2O_2$	319.9376	5	5	0	0
13789325		$C_8H_4Br_2N_2O_2$	319.9376	1	1	0	0

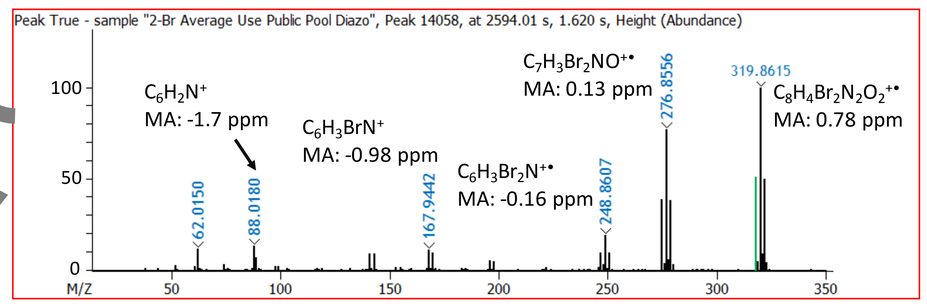
Elemental Composition Determined from Monoisotopic Mass

Elements from which to build the formula:

Element	Mass	Minimum	Maximum	Valences
C*	12.0000	1	50	4
H	1.0078	0	100	1
Br	78.9183	2	2	1
Cl	34.9689	0	10	1
I	126.9045	0	10	1
N	14.0031	0	10	3
O	15.9949	0	10	2
S	31.9721	0	10	2

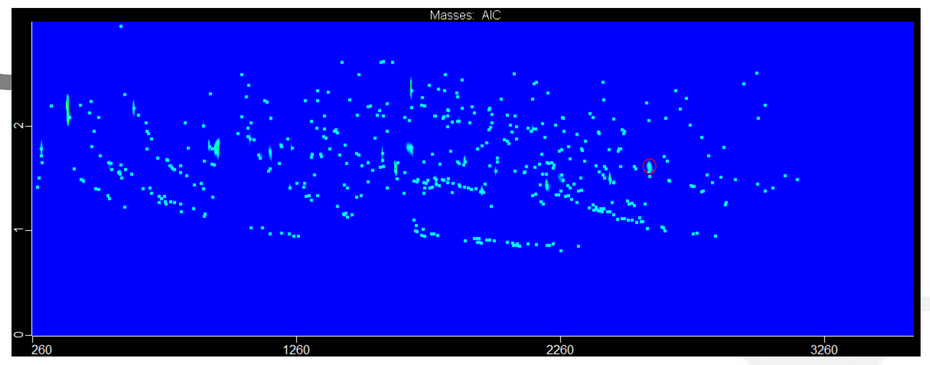
Search Mass: 317.8636516 Neutral Mass / m/z
+/- Mass Window: 3 mDa / ppm
Primary Selection Criteria: Isotope Pattern / Mass Difference

Hit	Formula	Expected Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)	Similarity	RDBE	
>1	C8H4Br2N2O2	317.8634	317.8637	0.78	993	7	✓
~~2~~	~~C14Br2N8~~	~~317.8641~~	~~317.8637~~	~~1.38~~	~~951~~	~~3~~	
~~3~~	~~C5H7Br2ClN3O~~	~~317.8639~~	~~317.8637~~	~~-0.75~~	~~824~~	~~2.5~~	



Classification with Peak Filters: Br_2 Class Compounds

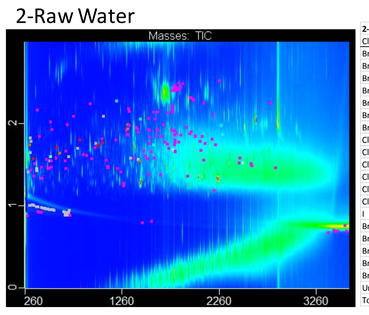
Analytical ion chromatogram (AIC) showing only the peaks that were classified as containing 2-Br, defined by the spectral filters (almost 500 peaks). Notice how even though the TIC is extremely complex, the AIC shows high quality chromatographic peaks determined automatically by the software. If we select a peak, in this case one of the most intense peaks by area, we can view the deconvoluted mass spectrum and library search results. Notice the high quality of the mass spectrum from a very complex region of the chromatogram.



Classification Summary Tables

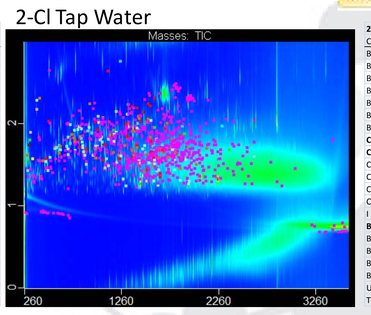
Area % as measured by the deconvoluted TIC for each class was compared for four sample types from Raw Water to Tap Water to Swimming Pool Water and Spa Water. The data show that the abundance of brominated compounds increased significantly in the swimming pool and spa treated with bromine as the disinfectant compared to the tap water used to fill the pools. Also, the tap water treated with chlorine had more chlorinated compounds than the untreated raw water [1].

2-Raw Water



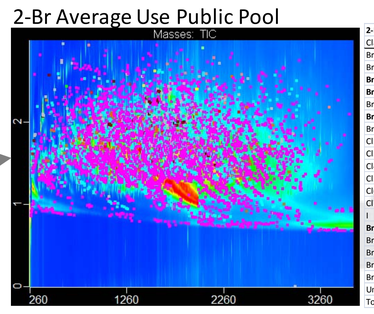
2-Raw Water Class	Area %
Br3Cl	0
Br2Cl	0
BrCl	0.015
Br3	0
Br4	0
Br2	0.022
Br5	0
Cl2	0.046
Cl3	0.06
Cl4	0
Cl5	0
Cl6	0
Cl7	0
I	0.062
Br	0.804
Br2Cl2	0
Br3Cl2	0
BrCl2	0
BrCl3	0
Unclassified	99.069
Total	100

2-Cl Tap Water



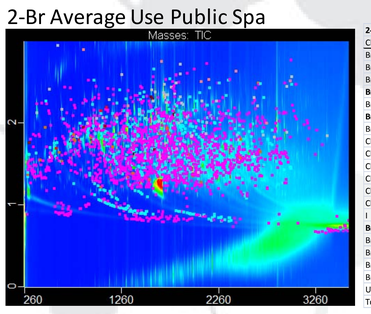
2-Cl Tap Water Class	Area %
Br3Cl	0
Br2Cl	0.047
BrCl	0.692
Br3	0.045
Br4	0
Br2	0.161
Br5	0
Cl2	**3.195**
Cl3	**2.415**
Cl4	0.265
Cl5	0.112
Cl6	0
Cl7	0
I	0.005
Br	**7.112**
Br2Cl2	0
Br3Cl2	0
BrCl2	0.119
BrCl3	0
Unclassified	90.882
Total	100

2-Br Average Use Public Pool



2-Br Average Use Publi Class	Area %
Br3Cl	0.025
Br2Cl	0.677
BrCl	**2.123**
Br3	**3.437**
Br4	0.172
Br2	**16.331**
Br5	0.007
Cl2	0.391
Cl3	0.309
Cl4	0.206
Cl5	0.218
Cl6	0.021
Cl7	0.021
I	0.057
Br	**41.146**
Br2Cl2	0.008
Br3Cl2	0.056
BrCl2	0.171
BrCl3	0.047
Unclassified	53.694
Total	100

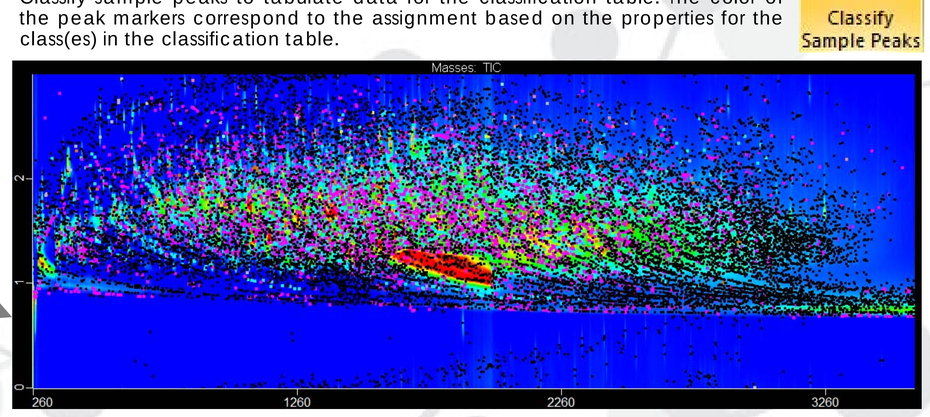
2-Br Average Use Public Spa



2-Br Average Use Publi Class	Area %
Br3Cl	0
Br2Cl	0.344
BrCl	0.313
Br3	**2.761**
Br4	0.105
Br2	**9.216**
Br5	0
Cl2	0.056
Cl3	0.073
Cl4	0
Cl5	0
Cl6	0
Cl7	0
I	0.008
Br	**18.016**
Br2Cl2	0
Br3Cl2	0.075
BrCl2	0.036
BrCl3	0.022
Unclassified	79.304
Total	100

Classification with Accurate Mass Peak Filters

Classify sample peaks to tabulate data for the classification table. The color of the peak markers correspond to the assignment based on the properties for the class(es) in the classification table.



Reference

1. Daiber, E.J. et al. **2016**. Environ Sci Technol. Progressive Increase in Disinfection Byproducts and Mutagenicity from Source to Tap to Swimming Pool and Spa Water: Impact of Human Inputs. http://pubs.acs.org/doi/ipdf/10.1021/acs.est.6b00808.

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