SPE-GCxGC-TOFMS for Detection of Disinfection By-Products and Endocrine Disruptors in Municipal Water, Residential Swimming Pools, and Purified Bottled Drinking Water

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INTRODUCTION

The chemicals used to treat drinking and swimming pool water can produce potentially toxic compounds known as disinfection by-products (DBPs). Numerous DBPs are known to have mutagenic and/or carcinogenic activity as well as reproductive/developmental effects. This application presents a screening procedure utilizing comprehensive two-dimensional gas chromatography-Time-of-Flight Mass Spectrometry (GCxGC-TOFMS) for the detection of DBPs and endocrine-disrupting compounds (EDCs) in water. Multiple samples from municipal water supplies, as well as drinking and swimming pool water, were prepared by solid-phase extraction (SPE) followed by replicate GCxGC-TOFMS analyses.

EXPERIMENTAL METHODS

SAMPLE PREPARATION

HLB CARTRIDGE

- Load 0.5 g of Supelco, Supel™-Select HLB resin (hydrophilic modified styrene polymer) into a 6 mL glass reaction tube with a Teflon frit (Supelco Cat. # 504394)
- Wash cartridge with 15–20 mL of Acetone/5% Methanol dropwise slowly 5 mL at a time
- Wash cartridge with 15–20 mL of Methylene chloride dropwise slowly 5 mL at a time
- Condition cartridge with 10 mL HPLC grade water/5% Methanol dropwise slowly 5 mL at a time
- Condition cartridge with 10 mL HPLC grade water dropwise slowly 5 mL at a time
- Pull vacuum for 10–15 minutes, seal top with Parafilm®, and store cartridges in a refrigerator until needed

SPE METHOD

- Extractions were conducted with a Supelco visiprep vacuum manifold equipped with a Large Volume Sampler
- Condition cartridge with 2 x 5 mL HPLC water/5% Methanol
- Condition cartridge with 2 x 5 mL HPLC water
- Remove cartridge from the vacuum manifold and attach the large volume sampler
- Load 1 L water sample onto the cartridge at 2–3 drops per second
- Dry the SPE cartridge for 10 minutes under vacuum
- Place a Pyrex® 15 x 125 mm test tube in the vacuum manifold for sample collection
- Elute the cartridge with 5 mL Acetone/5% Methanol slowly
- Follow by elution with 5 mL Methylene chloride slowly
- Remove sample collection tube and concentrate eluant to 150–200 µL with a speedvac or by nitrogen blowdown
- Load eluant into autosampler vial and analyze

Pegasus 4D GCxGC-TOFMS

METHODS

GCxGC Parameters

- Gas Chromatograph: Agilent 7890 equipped with a LECO dual stage, quad jet thermal modulator, secondary oven, and a GERSTEL MPS2 autosampler
- GC Primary Column: 30 m x 0.25 mm id. x 0.25 µm film thickness Rxi-5SilMS (Restek Corp.)
- GC Secondary Column: 1.25 m x 0.18 mm id. x 0.18 µm film thickness Rxi-17Sil-MS (Restek Corp.)
- Carrier Gas: Helium set @ 1.0 mL/min
- Injection Mode: Splitless
- Injection Volume: 1 µL
- Inlet Temperature: 250°C
- Primary Column Temperature Program: Initial temperature 30°C for 10 min ramped @ 6.0°C/min to 295°C held for 4 min
- Secondary Column Temperature Program: Initial temperature 40°C for 10 min ramped @ 6.0°C/min to 305°C held for4 min
- GCxGC Modulator Temperature Offset: 15°C
- Modulation Period: 5 seconds
- Transfer Line Temperature: 250°C
- Total Run Time: 58.17 min

Pegasus® 4D TOFMS Parameters

- Mass Range: 35–800 m/z
- Acquisition Rate: 200 spectra/s
- Ion source Temperature: 230°C
- Detector Voltage: 1425 V
- Acquisition Delay: 192 seconds

RESULTS

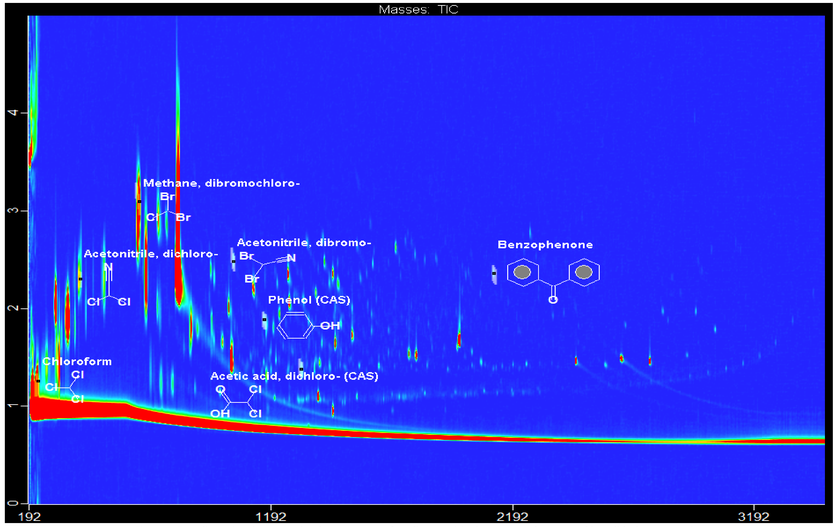
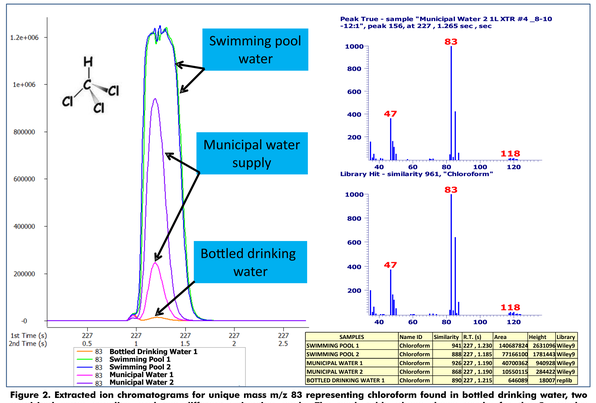


Figure 1. Two-dimensional contour plot chromatogram of a 1 liter municipal water sample prepared by solid-phase extraction. A 1 µL injection is displayed in the analysis by GCxGC-TOFMS.

DISINFECTION BY-PRODUCT CHLOROFORM COMPARISON



SAMPLES	Name ID	Similarity	R.T. (s)	Area	Height	Library
SWIMMING POOL 1	Chloroform	943	227 , 1.230	140687824	2631096	Wiley9
SWIMMING POOL 2	Chloroform	888	227 , 1.185	77166100	1781443	Wiley9
MUNICIPAL WATER 1	Chloroform	926	227 , 1.190	40700362	940928	Wiley9
MUNICIPAL WATER 2	Chloroform	868	227 , 1.190	10550115	284422	Wiley9
BOTTLED DRINKING WATER 1	Chloroform	890	227 , 1.215	646089	18007	replib

Figure 2. Extracted ion chromatograms for unique mass m/z 83 representing chloroform found in bottled drinking water, two municipal water supplies, and two different swimming pools. The peak table above shows results for the 5 samples represented chromatographically. Notice widely varying results from different water sources. In particular, the chloroform peak area for Swimming Pool 1 is 217 times greater than that for the bottled drinking water.

CHLOROFORM CALIBRATION

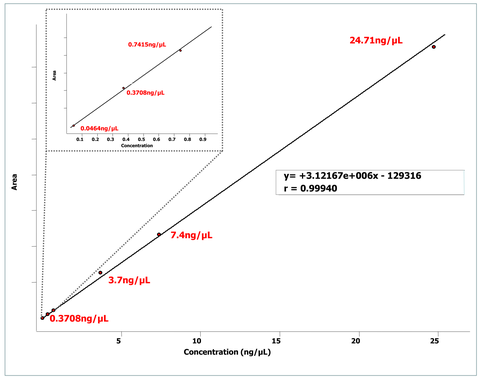


Figure 3. A six-point calibration curve was developed for chloroform from 46.4 picograms to 24.7 nanograms. The linear 1st order equation Pearson's "r" value was calculated at 0.9994.

DBPs and EDCs DETECTED

Disinfection By-Product Results Comparison with EPA Method 551.1 and Priority DBPs from the EPA 2005 National Occurrence Study List

Table 1. Combined results of the SPE-GCxGC-TOFMS analysis conducted for two municipal water supplies, two residential swimming pools, and a purified bottled drinking water source.

Halomethanes	Haloaldehydes
Chloroform	Dichloroacetaldehyde
Methane, bromo-	Bromochloroacetaldehyde
Methane, bromodichloro-	Trichloroacetaldehyde monhydrate
Methane, dibromochloro-	(Chloral hydrate)
Methane, tribromo	
Dichloroiodomethane	**Halonitromethanes**
Haloacetonitriles	Dichloronitromethane
	Bromochloronitromethane
Acetonitrile, bromochloro-	Trichloronitromethane (Chloropicrin)
Acetonitrile, chloro-	
Acetonitrile, dibromo-	**Haloamides**
Acetonitrile, dichloro-	
	Dibromoacetamide
Haloketones	Acetamide, 2,2-dichloro-
	Acetamide, 2,2,2-trichloro-
2-Propanone, 1,3-dichloro-	
2-Propanone, 1,1,3-trichloro-	**Haloacetic acids**
2-Propanone, 1-chloro-	
1,1,1,3,3-Pentachloropropanone	Acetic acid, dichloro-
2-Propanone, 1,1,3,3-tetrachloro-	Bromochloroacetic acid
2-Propanone, 1,1,1,3-tetrachloro-	Monochloroacetic acid
1-Bromo-1,1-dichloro-2-propanone	Trichloroacetic acid
	acetic acid, bromo-
VOCs and Miscellaneous DBPs	**Haloacids**
Benzyl chloride	3,3-Dichloropropenic acid
Trichloroethylene	
Chlorodibromoacetaldehyde	
Benzene, 1,4-dichloro-	

EDCs Found in Municipal Water, Swimming Pools, and Bottled Drinking Water Compared to the TEDX List of Potential Endocrine Disruptors

Table 2. Endocrine disruptors found in two municipal water supplies, two residential swimming pools, and a purified bottled drinking water source. The EDCs listed below are chemicals included in the Endocrine Disruptor Exchange (TEDX) list.

Name	R.T. (s)	Similarity	Area	UniqueMass	S/N	Library
Benzene (CAS)	262 , 1.435	845	4009119	78	6108.3	Wiley9
1,1'-Biphenyl (CAS)	1807 , 2.020	789	15184	154	287.41	Wiley9
Benzophenone	2112 , 2.365	818	104047	105	1251.3	replib
Phenol, p-tert-butyl-	1677 , 1.780	864	99384	135	1483.7	mainlib
Toluene	502 , 2.305	943	9473479	91	9374.3	replib
Bisphenol A	2657 , 2.950	612	19381	213	159.08	Wiley9
Naphthalene (CAS)	1527 , 2.015	702	17635	128	295.38	Wiley9
Phenol	1162 , 1.890	913	307236	94	1583.5	mainlib
Phenol, 4-(1,1,3,3-tetramethylbutyl)- (CAS)	2077 , 1.765	676	26230	135	517.82	Wiley9
p-Cresol	1342 , 1.845	718	18601	107	210.8	replib

CHLOROFORM QUANTIFICATION

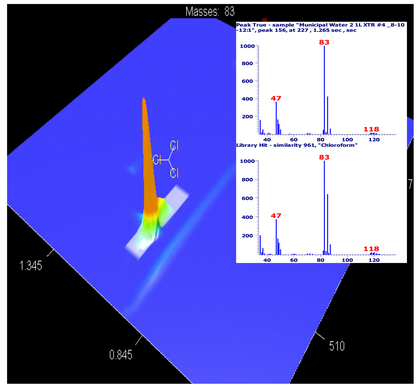


Figure 4. A six-point calibration curve was developed for chloroform from 46.4 pg to 24.7 ng. The concentration of the chloroform peak found in a 1 liter municipal water sample shown in the contour plot is back calculated to be 1.57 µg/L or 1.57 ppb.

Name	R.T. (s)	ng/uL	Similarity	Area	Height	Quant Masses	S/N	Library
Chloroform	227 , 1.265	10.47	887	32569822	3770271	83	96363	Wiley9

CONCLUSIONS

These SPE-GCxGC-TOFMS analyses identified 37 DBPs by comparison to EPA lists including Method 551.1 and the EPA 2005 DBP National Occurrence Study. Further data review compared to the TEDX list of EDCs found ten chemicals which are known endocrine-disrupting compounds. This work demonstrates a reliable and sensitive procedure for the untargeted detection of trace levels of DBPs and EDCs in disinfection treated and purified drinking water by solid-phase extraction (SPE) followed by GCxGC-TOFMS analysis.

A solid-phase extraction method was utilized using a hydrophilic modified styrene-based polymer for a broad range of compounds from aqueous samples. An optimized GCxGC method was developed using a conventional non-polar and mid-polarity column set. A TOFMS method was created which offers continuous full range non-skewed mass spectral information, True Signal Deconvolution®, and fast acquisition rates ideal for the characterization of DBPs, EDCs, and other contaminants in water.

This work emphasizes the need for instrumentation that will detect and identify sources of long-term environmental exposure to DBPs and EDCs that can lead to ecological destruction and serious health effects. The application of GCxGC-TOFMS for this work presents a sensitive and robust instrumental option for the detection of DBPs and EDCs, as well as other untargeted contaminants in treated water.

For further information regarding this study contact the authors at john_heim@leco.com

REFERENCES

(1) EPA Method 551.1

(2) Combining Mass Spectrometry and Toxicology for a Multi-Country European Epidemiologic Study on Drinking Water Disinfection By-Products, Richardson, S., S. Anduri, M. Bloodgood, M. Plewa, C. Jeang, E. Wagner, M. Nieuwenhuijsen, M. Kogevinal, C. Villanueva, W. Luo, L. Isabelle, AND J. Pankow. Presented at ASMS Conference, May 20 - 24, 2012. http://www.asms.org/