Nontarget screening of halogenated disinfection by-products in swimming pool water by LC-HRMS

Schmalz, C. and Zwiener, C.

Environmental Analytical Chemistry, Eberhard-Karls-Universität Tübingen, Hölderlinstr. 12, 72074 Tübingen, Germany

Introduction

Disinfection of swimming pool water with chlorine is worldwide the most commonly used method and is a compromise between hygienic safety and the effects of toxic disinfection by-products (DBPs). A recent study identified more than 100 DBPs in swimming pool water by GC-MS, many of them not previously identified [1]. Much less is known on the polar DBPs. LC coupled with high resolution mass spectrometry enables to determine sum formulae and hence to do screening for unknown compounds. However, the availability of LC-MS libraries and especially entries of transformation products are very limited. Statistical analysis and manual interpretation of mass fragmentation have to be used [2].

LC-Q-TOF Analysis
MS-Fullscan

↓

Data Extraction
Molecular Feature Extraction

↓

Sum Formulae
Generate Formulae

↓

Statistical Analysis
Mass Profiler

↓

Data Base
Search for suspects

↓

***In silico* fragmentation**
Targeted MS/MS

↓

Identification
Spectral library, MetFrag
Molecular Structure Correlator

Materials and Methods

Water from public swimming pools with different treatment steps and bather loads were taken. The samples were acidified (pH2), pre-concentrated by solid phase extraction on LiChrolut ENV+ by a factor of 5000 and analyzed by LC-ESI-QTOF-MS (Agilent iFunnel 6550). Accurate mass and retention time data were processed in a non-target approach.

Results

Molecular feature extraction

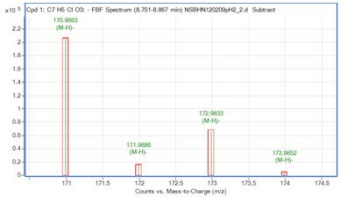
Number of compounds (Score > 70 %)		
	Pool water	Filling water
Molecular features	6400	2700
Sum formulae (C,H, Br, Cl, N,O, S)	1800	900
≥ 1 chlorine	630	245
≥ 1 bromine	190	80

Sum formulae and isotopic pattern

Retention time (min)	Exact mass	Sum formula	Score
8.80	171.9934	C7 H5 Cl O3	94.6

Isotopes

m/z	m/z (Calc)	Diff (ppm)	Height %	Height % (Calc)
170.9863	170.9854	-5.14	100	100
171.9886	171.9888	1.36	8.8	7.7
172.9833	172.9827	-3.72	31.8	32.9
173.9852	173.986	4.61	2.9	2.5

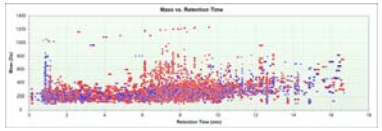


The precision (score) of the sum formulae is calculated by comparison of the exact and the theoretical mass including the isotopic patterns.

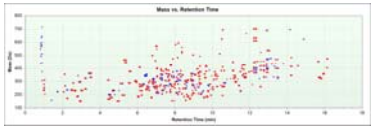
Statistical analysis

Pattern Matching (Mass Profiler Software)

Compounds (n=3)
- **blue** Compounds in filling water (not relevant)
- **red:** Compounds in pool water (relevant)



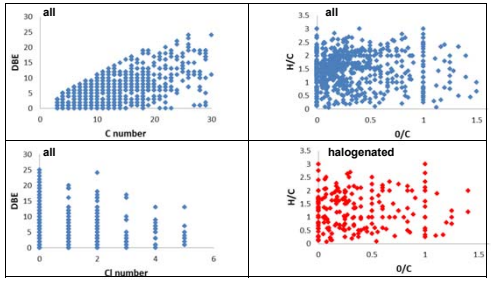
Compounds with molecular features
- 650 down regulated features (filling water)
- 3500 up regulated features (pool water)



Compounds with ≥ 1 chlorine
- 50 down regulated features (filling water)
- 300 up regulated features (pool water)

Degree of unsaturation (DBE) **Van Krevelen-Plot**

Blue: All compounds with sum formulae (C,H,Br,Cl,N,O,S)
Red: Halogenated compounds with at least 1 chlorine



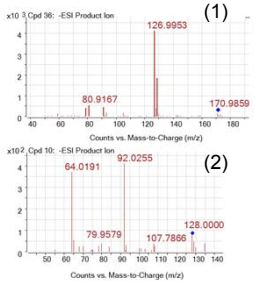
→ DBE and oxidation similar for all and the halogenated compounds
→ Increasing chlorination degree results in decreasing number of DBE

Data base search

Mass	Sum formulae	Name	Class	Reference
163.9876	C5 H5 Cl O4	(E)-2-Chloro-3-methylbutenedioic acid	DBP	[1]
149.9717	C4 H3 Cl O4	2-Chlorobutenedioic acid	DBP	[1]
145.9090	C2 H Cl3 O	Trichloroacetaldehyde	DBP	[1]
254.1671	C18 H22 O	3-(4-Methylbenzyliden) camphor	UV-Filter	[3]
290.1882	C18 H26 O3	2-Ethylhexyl-4-methoxy-trans-cinnamate	UV-Filter	[3]
204.1520	C14 H20 O	Lilial	Fragrance	[4]
152.1205	C10 H16 O	Camphor	Fragrance	[4]
186.0084	C8 H7 Cl O3	Cl-Methylparaben	Preservative	[5]
171.9934	C7 H5 Cl O3	Cl-Hydroxybenzoic acid	Preservative	[6]

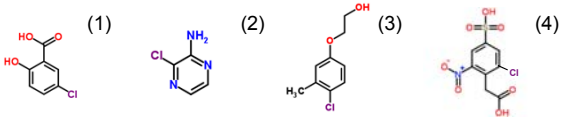
In-silico fragmentation

Structure information (MSMS) for 70 chlorinated compounds (n = 3, Score > 90%)



Proposed structures with additional fragment information (**Molecular Structure Correlator**)

Tentative compounds	ID (Chemspider)	Source
Chloro-2-hydroxybenzoic acid (1)	9075	Preservative
Chloro-2-pyrazinamine (2)	243075	??
Chloro-methylphenoxy-ethanol (3)	120319	Surfactant?
(Nitro-sulfo-chloro-phenyl)acetic acid (4)	no entry	Surfactant?



Conclusions and Outlook

→ In swimming pool water samples sum formulae of more than 300 halogenated compounds have been found.
→ Decreased number of DBE with increasing chlorination degree suggests these compounds as DBPs.
→ Halogenation products of preservatives (salicylic acid) and surfactants (sulfonic acid derivatives) were tentatively identified.
→ Confirmation of the proposed halogenated compounds requires standards to be generated from available precursors.

Acknowledgement: This work is funded by the BMBF (02WT1090)

References:
[1] Richardson SD, et al. (2010) Environ Health Perspect 118, 1523-1530.
[2] Zedda M, Zwiener C. (2012) Anal Bioanal Chem 403 2493-502.
[3] Zwiener C, et al. (2007) Environ Sci Technol 41, 363-372.
[4] Brausch JM, Rand, GM (2011) Chemosphere 22, 1518-1532.
[5] Terasaki M, Makino M(2008) Int J Environ Anal Chem 88 911-922.
[6] Quintana JB, Rodil R (2010) Wat Res 44, 243-255.

Contact: Email: christina.schmalz@uni-tuebingen.de
Tel: +49-07071-2977551