Analysis of Haloacetic Acids by IC-MS/MS in Drinking Water

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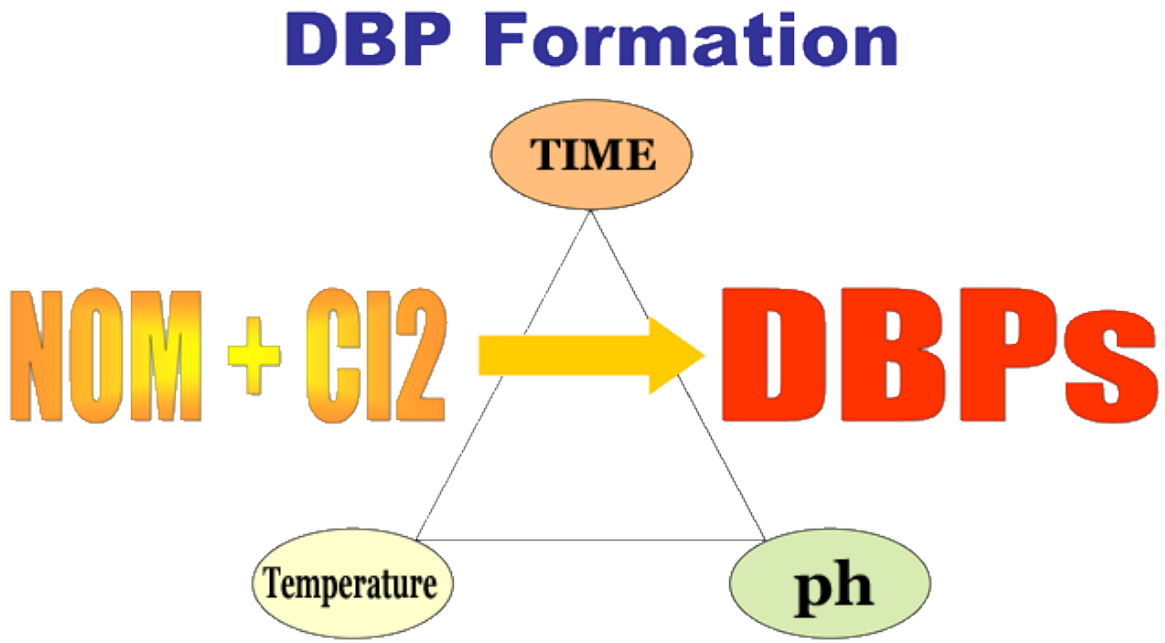
Disinfection Byproducts

Definitions

- The reaction of disinfectants used in water treatment with naturally occurring matter (organic and inorganic) which leads to formation of other products (byproducts)



Disinfection Byproducts

Major Classes in water [1]

- Account for 20-60% of DBPs during chlorination

- Trihalomethanes (THMs)
- Haloacetic acids (HAAs)

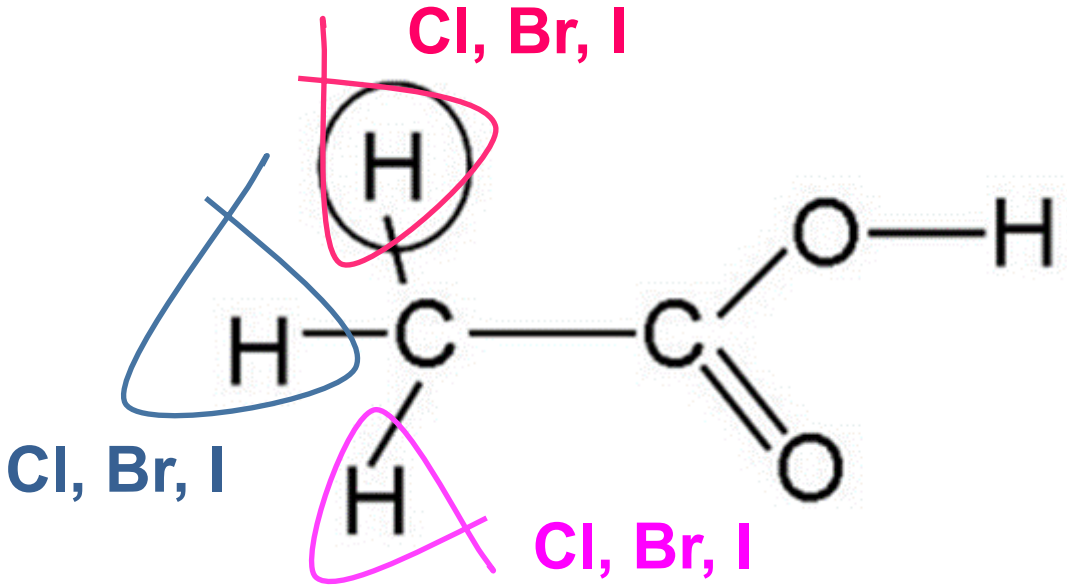
} >50% on a wt. basis

- Haloacetonitriles
- Haloketones
- Chloral hydrate
- Chloropicrin

[1] *USEPA. 1997. 600-R-97-122. Research Plan for Microbial Pathogens and Disinfection By-Products in Drinking Water*

Haloacetic acids (HAAs)

Structure



pK_a: 0.5-2.9

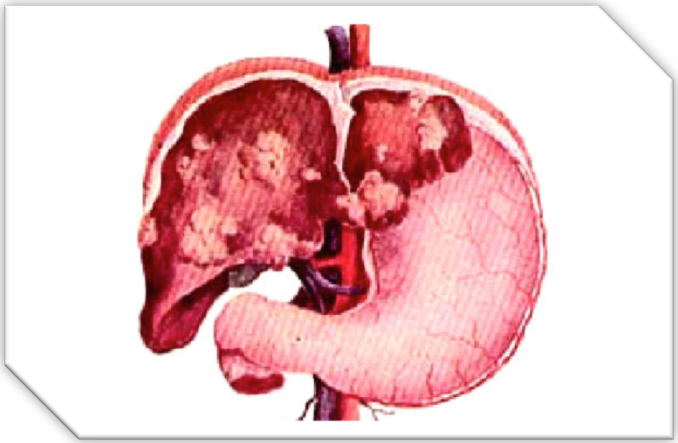
Log P: 0.2-1.5

Toxicological Relevance

Toxicity

- Haloacetic acids
  - Skin and eye irritation
  - Liver tumors
  - Neurological disorders
  - Possible human carcinogen

- Bromate
  - Nausea, vomiting, abdominal pain
  - Thyroid, liver and kidney cancer
  - Human carcinogen



- Dalapon
  - Kidney effects

Acute effects; Chromic effects

Occurrence

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Steelton drinking water tests positive for contaminant

According to the letter, testing completed on November 14 showed that the system exceeded the standard or maximum contaminant level for haloacetic acids and trihalomethanes, a disinfection by-product.

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Last Updated: Friday, 19 March, 2004, 14:19 GMT

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Coke recalls controversial water

Coca-Cola is to recall all bottles of its Dasani water in the UK, after levels of bromate were found to exceed legal levels.

The recall is an embarrassment for the drinks giant, which has faced criticism for selling what is treated and purified tap water.

Dasani is the second biggest selling

The Telegraph

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Coke's purified tap water is recalled in chemical alert

Haloacetic acids

Class	Compound	Acronym	MCL (ug/L)
Carcinogen	Bromate	BrO_3^-	10
HAA_9	Monochloroacetic acid	MCAA	60
	Dichloroacetic acid	DCAA	
	Trichloroacetic acid	TCAA	
	Monobromoacetic acid	MBAA	
	Dibromoacetic acid	DBAA	
	Bromochloroacetic acid	BCAA	-
	Bromodichloracetic acid	BDCAA	
	Dibromochloroacetic acid	DBCAA	
	Tribromoacetic acid	TBAA	
Emerging HAAs	Monoiodoacetic acid	MIAA	-
	Chloroiodoacetic acid	CIAA	
	Bromoiodoacetic acid	BIAA	
	Diiodoacetic acid	DIAA	
Herbicide degradate	Dalopon	Dal	

Iodinated-HAAs

ELSEVIER

Mutation Research/Reviews in Mutation Research

Volume 636, Issues 1–3, November–December 2007, Pages 178–242

The Sources and Potential Hazards of Mutagens in Complex Environmental Matrices - Part II

Review

Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research

Susan D. Richardson[a], Michael J. Plewa[b], Elizabeth D. Wagner[b], Rita Schoeny[c], David M. DeMarini[d]

Genotoxicity:
I-DBPs >> Br-DBPs > Cl-DBPs

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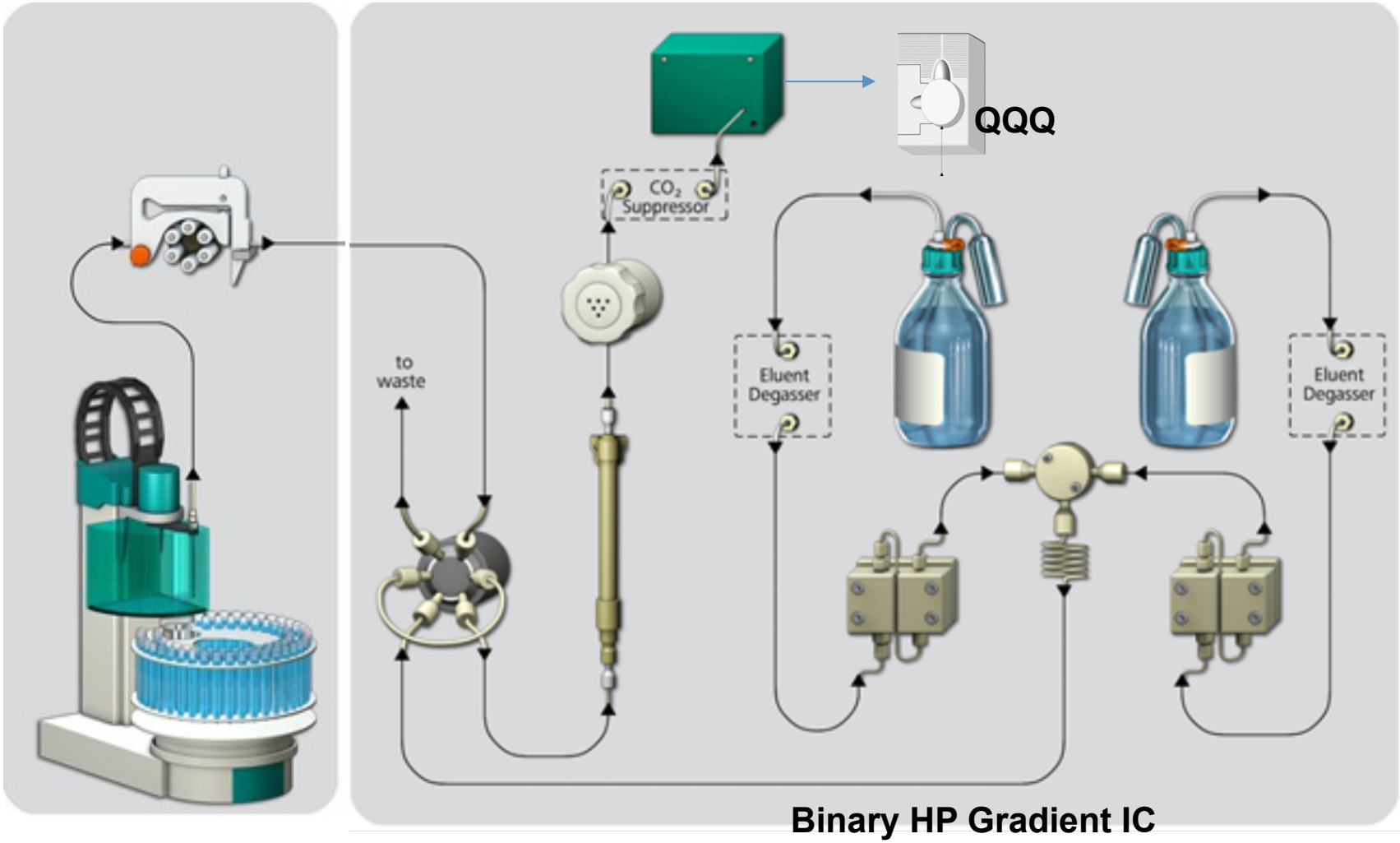
The formation and control of emerging disinfection by-products of health concern

Stuart W. Krasner

DOI: 10.1098/rsta.2009.0108 . Published 7 September 2009

IC/MSMS Configuration

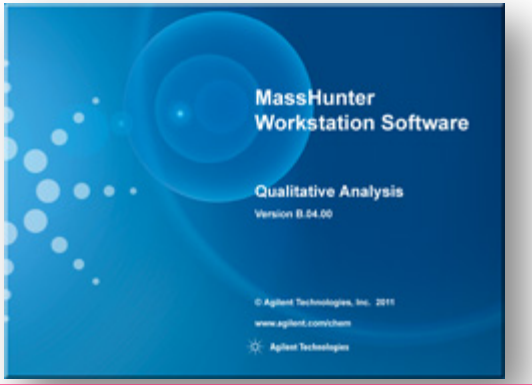


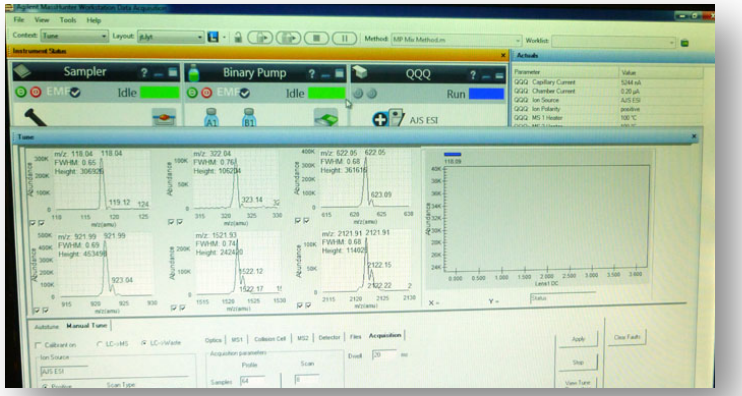
Binary HP Gradient IC

IC-MS/MS

IC-MS/MS Interface

MagIC Net





Metrohm to Agilent interface *Agilent MassHunter Platform*

IC Conditions

Method

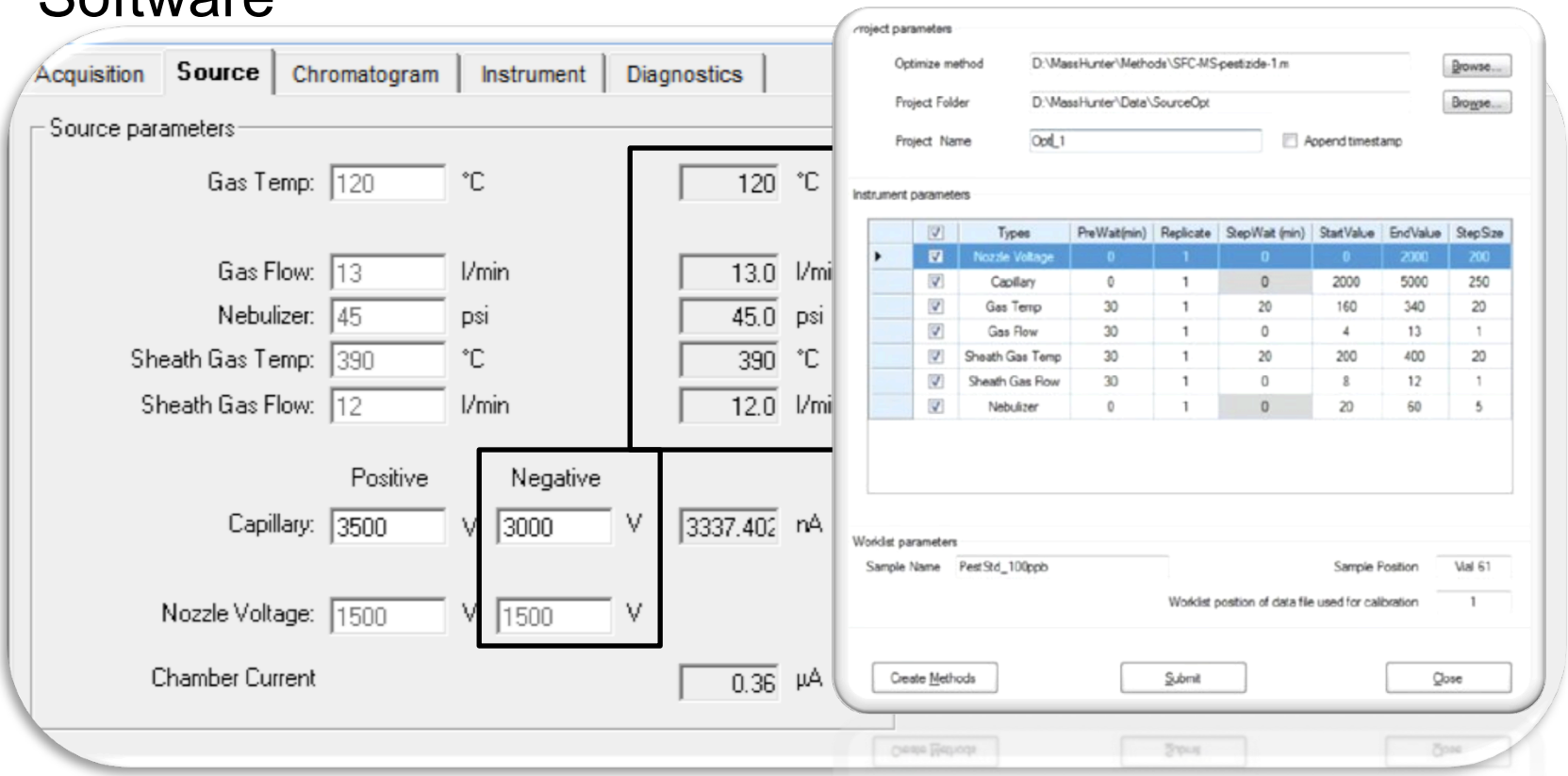
- Column: Metrosep A Supp 7 (250/4.0)
- Column Temperature: 45^{O}C
- Solvent A: [85/15: HPLC Water/ACN] + 50 mM KOH + 7 mM Na_2CO_3;
- Solvent B: HPLC Water

Time (min)	Gradient (%A)
0.0	20
2.0	20
12	95
16	95
17	20
18.5	20

Mass Spectrometer

6490 Agilent MS/MS

- All parameters optimized using Agilent SourceOptimizer Software



Compound Optimization

Transitions

Compound	Abv.	Precursor Ion	Product Ion	Collision Energy
Bromate	BrO_3^-	126.9	110.8	24
Bromate	BrO_3^-	126.9	95	36
Bromochloroacetic acid	BCAA	173	128.9	8
Bromochloroacetic acid	BCAA	173	80.9	24
Bromodichloroacetic acid	BDCAA	163	81	8
Bromolodoacetic acid	BIAA	262.8	218.7	8
Chlorodibromoacetic acid	CDBAA	206.9	81	8
Chlorodibromoacetic acid	CDBAA	206.9	78.9	8
Chloroiodoacetic acid	CIAA	218.9	126.9	20
Dalapon	DAL	141	97	6

Compound Optimization

Transitions

Compound	Abv.	Precursor Ion	Product Ion	Collision Energy
Dibromoacetic acid	DBAA	216.8	173	8
Dichloroacetic acid	DCAA	127	83	6
Diiodoacetic acid	DIAA	310.8	266.6	4
Monobromoacetic acid	MBAA	137	79	6
Monochloroacetic acid	MCAA	93	35	6
Monoiodoacetic acid	MIAA	184.9	126.7	20
Tribromoacetic acid	TBAA	250.9	78.9	20
Trichloroacetic acid	TCAA	163	119	8
Trichloroacetic acid	TCAA	117	34.9	8

Compound Optimization

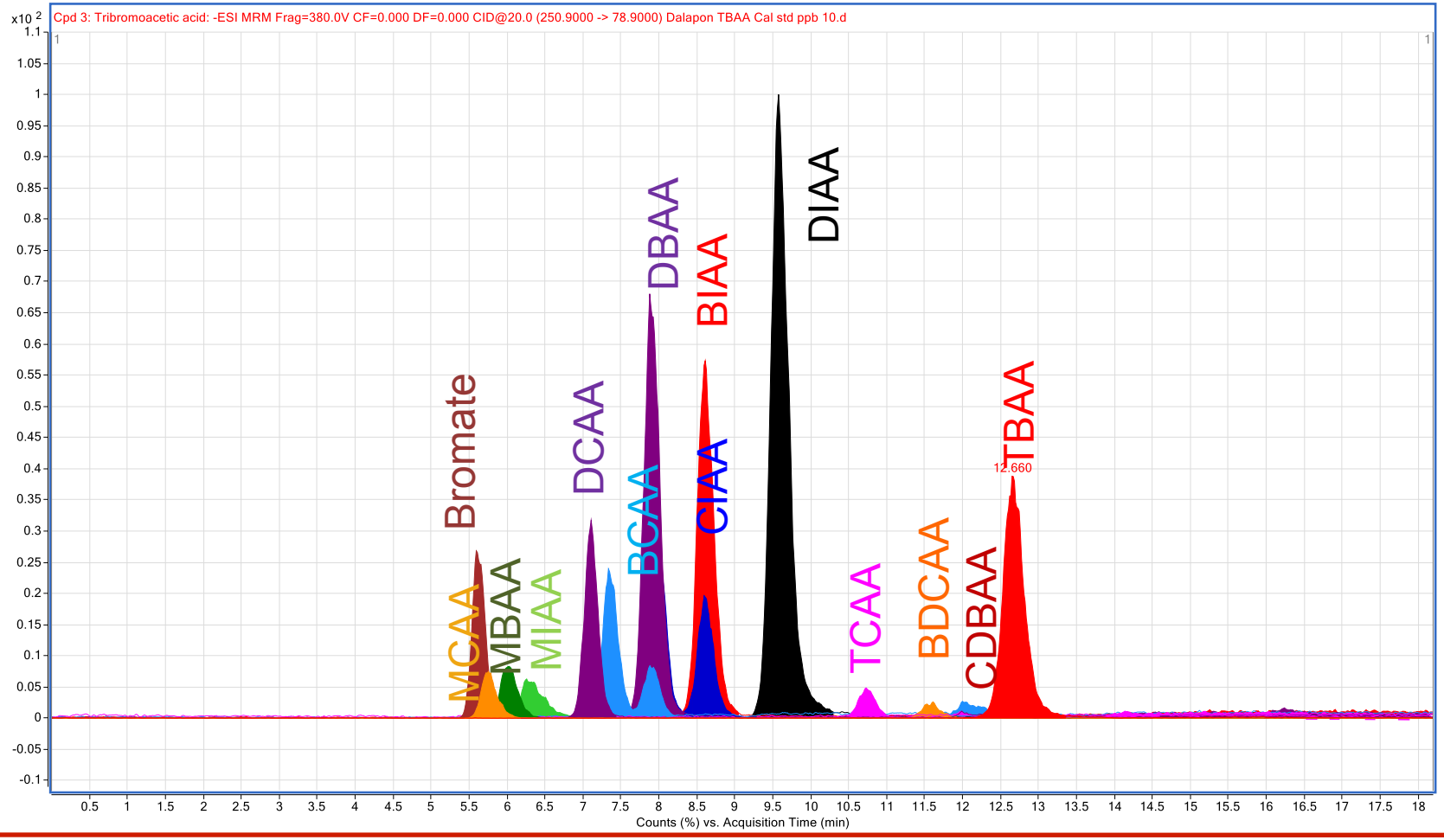
Internal Standards

Compound	Abv.	Precursor Ion	Product Ion	Collision Energy	Retention Time (min)	
Trichloroacetic acid $^{13}C_2$	TCAA $^{13}C_2$	118	34.9	8	10.6	TBAA TCAA BIAA BDCAA CDBAA
Dichloroacetic acid $^{13}C_2$	DCAA $^{13}C_2$	128	84	6	7.1	DCAA DBAA DIAA
Monobromoacetic acid $^{13}C_1$	MBAA $^{13}C_1$	138	79	6	5.9	MBAA MIAA Bromate
Monochloroacetic acid $^{13}C_2$	MCAA $^{13}C_2$	94	35	6	5.6	MCAA

Spiked at 10 µg/L in all samples

Chromatography

10 µg/L standard in Mili-Q water



Limits of Detection/Quantification

Compound	LOD (S/N>3)	LOQ (S/N>10)
BrO_3^-	0.1*	0.1
BCAA	0.1*	0.25
BDCAA	0.25	0.5
BIAA	0.1*	0.1
CDBAA	0.1	0.25
CIAA	0.1*	0.1
DAL	N.A	N.A
DBAA	0.1	0.25
DCAA	0.1*	0.1
DIAA	0.1*	0.1
MBAA	0.1*	0.1
MCAA	0.1*	0.1
MIAA	0.1	0.1
TBAA	5	10
TCAA	0.1*	0.1

*** S/N >10 at lowest standard (0.1 µg/L)**

S/N at 0.1 µg/L

Compound	LOD (S/N>3)
BrO_3^-	225
BCAA	3.3
BDCAA	-
BIAA	13
CDBAA	4.9
CIAA	17
DAL	N.A
DBAA	3.7
DCAA	193
DIAA	10
MBAA	325
MCAA	17
MIAA	85
TBAA	-
TCAA	205

If 2 transitions present, most abundant selected

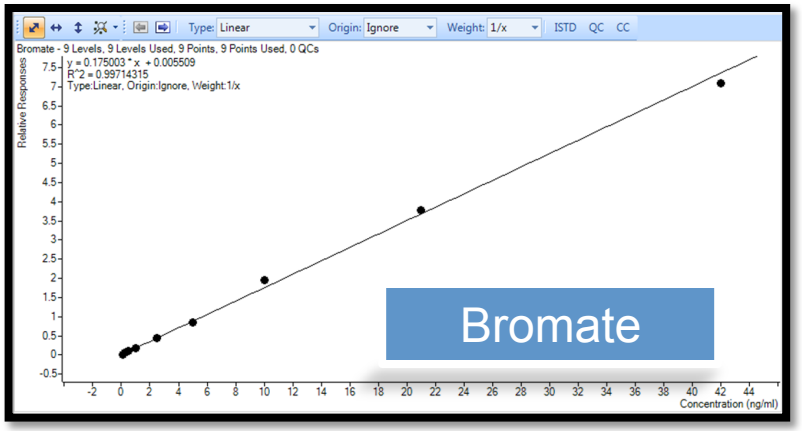
Method Reporting Limit (MRL)

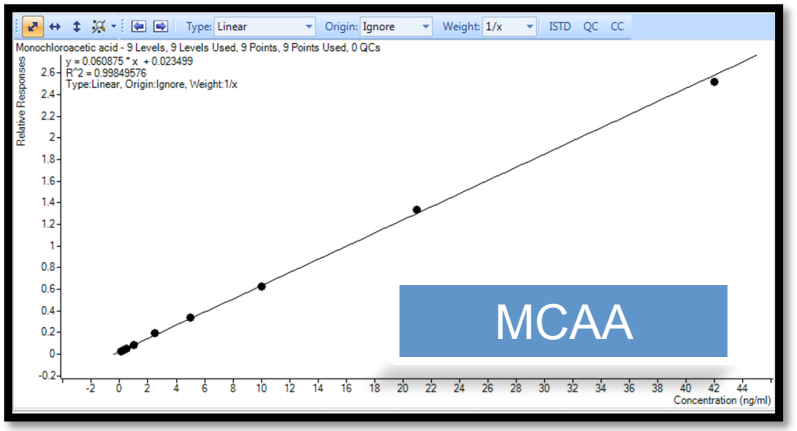
Based on Glaser et al. (n=7)

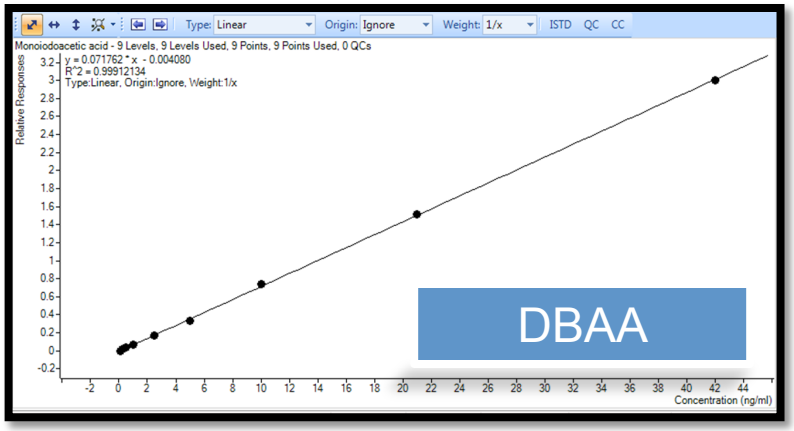
Compound	MRL (ug/L)	Fortification level (ug/L)	Compound	MRL (ug/L)	Fortification level (ug/L)
BrO_3^-	0.08	0.25	DCAA	0.10	0.25
BCAA	0.10	0.25	DIAA	0.09	0.25
BDCAA	0.24	0.5	MBAA	0.11	0.25
BIAA	0.09	0.25	MCAA	0.09	0.25
CDBAA	0.16	0.25	MIAA	0.10	0.25
CIAA	0.04	0.25	TBAA	3.5	10
DAL	0.08	0.25	TCAA	0.36	0.5
DBAA	0.09	0.25			

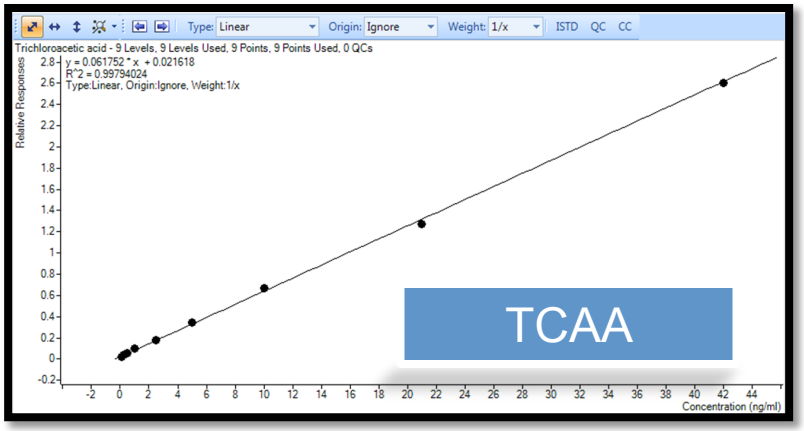
Linearity

Calibration curves from MRL – 40 µg/L









Linearity

Compound	R^2
BrO_3^-	0.9971
BCAA	0.9989
BDCAA	0.9986
BIAA	0.9980
CDBAA	0.9978
CIAA	0.9987
DAL	0.9976
DBAA	0.9981
DCAA	0.9977
DIAA	0.9979
MBAA	0.9972
MCAA	0.9984
MIAA	0.9991
TBAA	0.9957
TCAA	0.9979

Excellent linearity. R^2 >0.995 for all compounds

Reproducibility

Intra-day:3 samples spiked at 10 ppb tested every 4 hours

Inter-day:3 samples prepared daily & spiked at 10 ppb tested every day

Compound	Intra-day (RSD)	Inter-day (RSD)	Compound	Intra-day (RSD)	Inter Day (RSD)
BrO_3^-	2.1	5.1	DCAA	2.7	3.2
BCAA	3.2	4.7	DIAA	3.4	6.9
BDCAA	3.1	5.6	MBAA	1.2	4.7
BIAA	1.1	5.7	MCAA	0.9	3.4
CDBAA	1.6	5.7	MIAA	1.6	5.8
CIAA	0.9	4.4	TBAA	2.7	7.3
DAL	3.7	6.3	TCAA	4.4	6.1
DBAA	2.2	6.1			

Real Samples

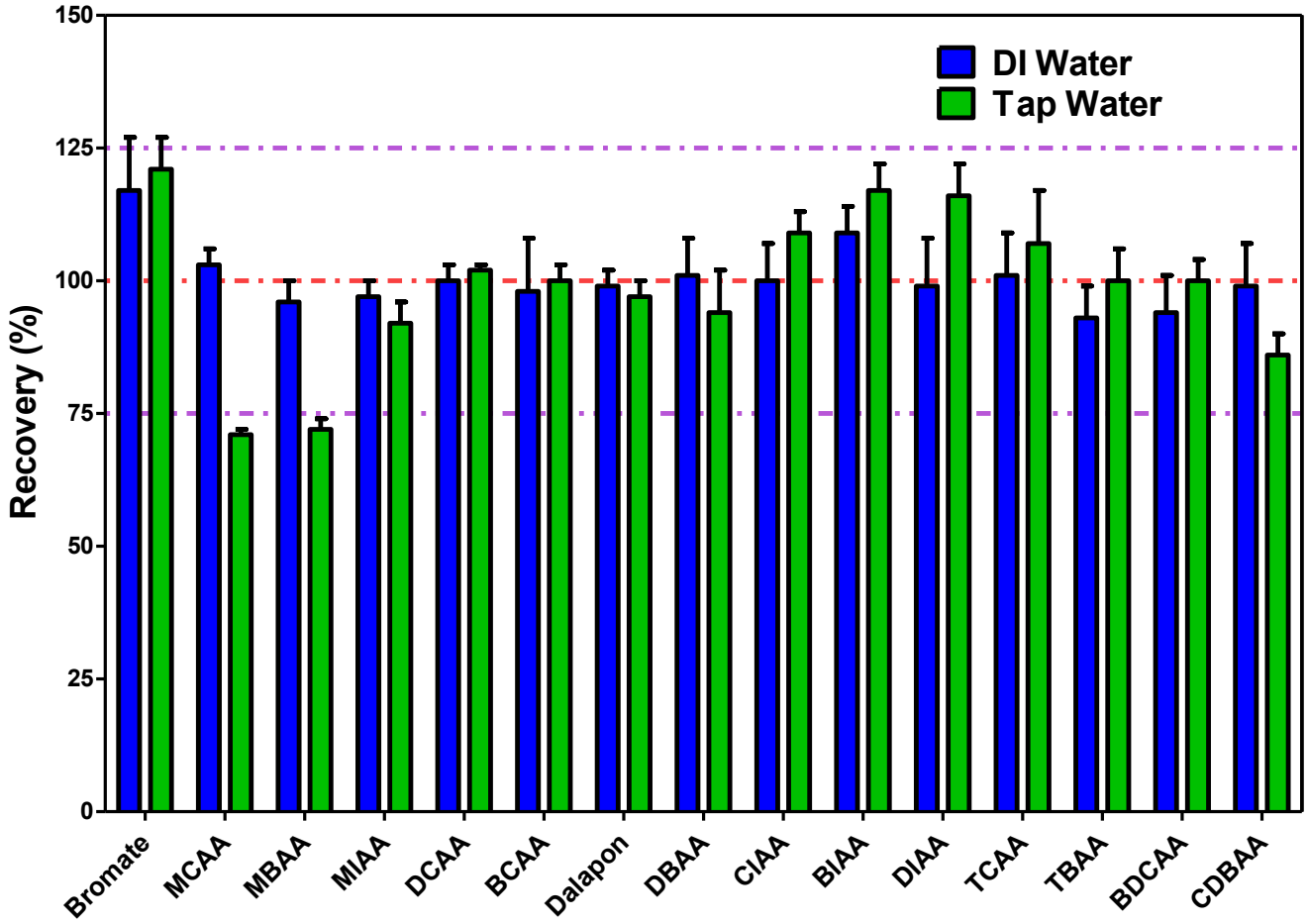
Tap water matrix spike recoveries

Compound	DI water (%)	Tap water (%)	Compound	DI water (%)	Tap water (%)
BrO_3^-	117±10	121±6	DCAA	100±3	102±1
BCAA	98±10	100±3	DIAA	99±9	116±6
BDCAA	94±7	100±4	MBAA	96±4	72±1
BIAA	109±5	117±5	MCAA	103±3	71±1
CDBAA	99±8	121±6	MIAA	97±3	92±4
CIAA	100±7	109±4	TBAA	93±6	100±6
DAL	99±3	97±3	TCAA	101±8	107±10
DBAA	101±7	94±8			

4 replicate samples spiked at 10 µg/L

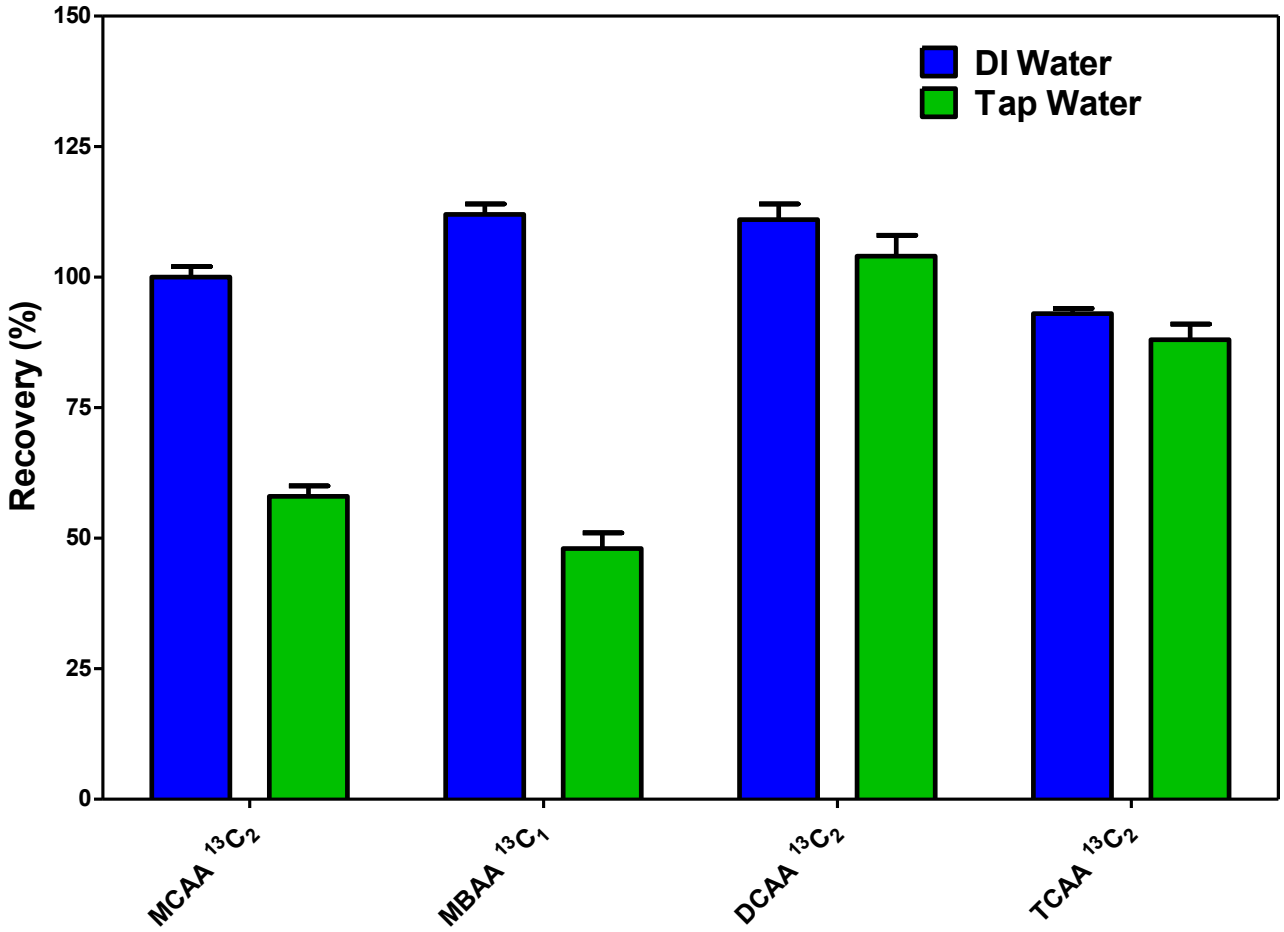
Real Samples

DI & Tap water matrix spike recoveries



Internal Standards

Matrix spike recoveries



10 µg/L IS spiked into each sample

Conclusions

- IC-MS/MS is a robust analytical technique for analysis of HAAs, bromate and Dalapon in drinking and surface waters.
- Statistical MRLs of 0.8-3.5 µg/L achieved with 12/15 compounds having sub 0.2 µg/L.
- Minimal sample preparation and rapid analysis time (<20 min) were achieved.
- Very good linearity and matrix spike recoveries for all 15 compounds were observed.
- In our work, we have NOT observed any degradation of MCIAA as illustrated in USEPA method

Acknowledgements

- JoAnne Barcelleano – U of Ariz.
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Thank You

Questions?