Support Information

Title: Emerging DBP quantification method for wastewater reuse: trace level assessment using tandem mass spectrometry

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Table S1. MRM transitions in the MSMS method. DBPs are separated by chemical class.

DBP	Fragment	Precursor Ion (m/z)	Fragment	Q Ion (m/z)	Fragment	q Ion (m/z)
CAN	$[CH_2ClCN]^+$	75.0	$[CHCl]^+$	48.0	$[CH_2CN]^+$	40.1
BAN	$[CH_2BrCN]^+$	120.9	$[CH_2CN]^+$	40.1	$[CH_2CN]^+$	41.1
IAN	$[CH_2ICN]^+$	166.9	$[CH_2CN]^+$	40.1	$[CH_2CN]^+$	41.1
DCAN	$[CHClCN]^+$	73.9	$[CCl]^+$	47.0	$[CHCN]^+$	40.1
DBAN	$[CHBrCN]^+$	117.9	$[CBr]^+$	90.9	$[CHCN]^+$	40.1
BCAN	$[CHClCN]^+$	73.9	$[ClC]^+$	47.0	$[CHCN]^+$	40.1
TCAN	$[CCl_2CN]^+$	107.8	$[CClCN]^+$	72.9	$[CCl]^+$	47.0
DCNM	$[CHCl_2]^+$	82.9	$[CHCl]^+$	48.0	$[CCl]^+$	47.0
DBNM	$[CHBr_2]^+$	172.8	$[CHBr]^+$	91.9	$[CHBr]^+$	93.9
BCNM	$[CHBrCl]^+$	128.9	$[CHCl]^+$	48.0	$[CCl]^+$	47.0
BDCAld	$[CHCl_2]^+$	82.9	$[CCl]^+$	46.9	$[CHCl]^+$	48.0
DBCAld	$[CHBrCl]^+$	128.9	$[CHCl]^+$	48.0	$[ClC]^+$	47.0
TBAld	$[CHBr_2]^+$	172.8	$[CHBr]^+$	91.9	$[CHBr]^+$	93.9
11DCP	$[CHCl_2]^+$	82.9	$[CCl]^+$	47.0	$[CHCl]^+$	48.0
13DCP	$[CH_2ClCO]^+$	77.0	$[CH_2Cl]^+$	49.0	$[CHCl]^+$	48.0
111TCP	$[Cl_2CCOCH_3]^+$	124.9	$[CCl_2CH_3]^+$	97.0	$[CHCl_2]^+$	82.9
113TCP	$[CH_2ClCO]^+$	77.0	$[CH_2Cl]^+$	49.0	$[CCl]^+$	47.0
1B11DCP	$[Cl_2CCOCH_3]^+$	124.9	$[CCl_2CH_3]^+$	97.0	$[CH_3CO]^+$	43.1
1133TeCP	$[CHCl_2]^+$	82.9	$[CCl]^+$	47.0	$[CHCl]^+$	48.0
DCIM	$[CHICl_2]^+$	209.9	$[CHCl_2]^+$	82.9	$[CHCl_2]^+$	84.9
BCIM	$[CHIBrCl]^+$	255.9	$[CHBrCl]^+$	128.8	$[CHBrCl]^+$	130.8
DBIM	$[CHBr_2]^+$	172.8	$[CHBr]^+$	91.9	$[CHBr]^+$	93.9
CDIM	$[CHICl]^+$	174.9	$[CHCl]^+$	48.0	$[CCl]^+$	47.0
BDIM	$[CHIBr]^+$	218.8	$[CHBr]^+$	91.9	$[CHI]^+$	140.0
TIM	$[CHI_2]^+$	266.8	$[CHI]^+$	140.0	$[I]^+$	127.0
I.S.	$[CH_2BrCHCH_3]^+$	120.9	$[CH_2Br]^+$	92.9	$[H_4C_3]^+$	41.1

Q: quantification; q: qualification

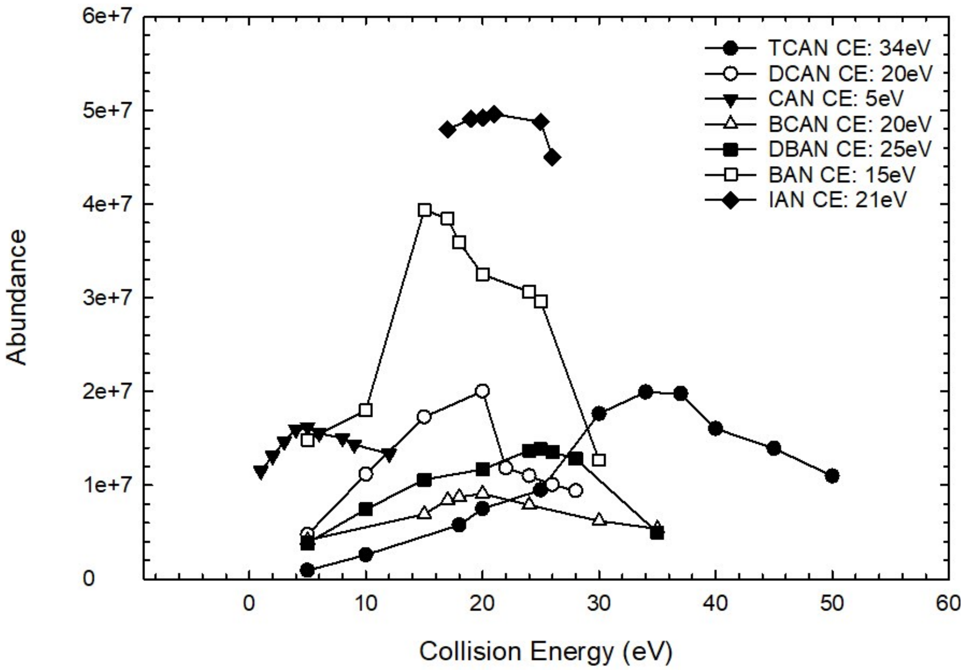

Figure S1. Collision energy manual optimization for haloacetonitriles.

Table S2. Conditions of each variable during the sample volume optimization

Variable	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Sample Volume (mL)	100	50	50	10
Organic Solvent (mL)	5 x 3	5 x 3	5 x 3	3 x 3
Sodium Sulfate (g)	30	15	15	3
Shake Time (min)	15	15	15	15
Rest Time (min)	15	15	15	15
Final Extract Volume (μL)	200	200	100	200

Table S3. Recovery percentage of each DBP spiked at 100 ng L^{-1} for each experiment.

DBP	Experiment 1	Experiment 2	Experiment 3	Experiment 4
CAN	N.D.	196	N.D.	127
BAN	N.D.	N.D.	N.D.	121
IAN	83	32	63	108
DCAN	90	45	71	91
DBAN	96	45	70	153
BCAN	93	44	68	90
TCAN	15	23	50	34
DCNM	99	51	78	109
DBNM	126	49	76	78
BCNM	104	46	71	93
BDCAld	90	46	81	88
DBCAld	93	42	76	107
TBAld	99	37	68	112
11DCP	87	N.D.	N.D.	109
13DCP	88	N.D.	N.D.	123
111TCP	N.D.	N.D.	N.D.	63
113TCP	82	2.7	4.0	134
1B11DCP	81	2.0	2.5	85
1133TeCP	87	N.D.	N.D.	138
DCIM	78	35	57	88
BCIM	66	28	49	72
DBIM	86	40	67	70
CDIM	94	37	64	53
BDIM	92	36	64	52
TIM	92	32	59	4

N.D. means not detected.

Table S4. Percent recovery, standard deviation (STD), and relative standard deviation (RSD) values of final extraction method in triplicate with 100 ng/L DBPs in water.

DBP	Percent Recovery (%)	STD (%)	RSD(%)
CAN	126.8	8.9	7.0
BAN	120.8	10.7	8.9
IAN	108.4	3.8	3.5
DCAN	91.4	1.2	1.3
DBAN	153.1	10.7	7.0
BCAN	89.2	7.9	8.8
TCAN	34.1	3.0	8.7
DCNM	109.2	8.0	7.4
DBNM	77.7	5.5	7.1
BCNM	92.9	10.5	11.3
BDCAld	87.7	25.7	29.3
DBCAld	106.6	2.1	2.0
TBAld	111.7	9.2	8.3
11DCP	108.5	7.9	7.3
13DCP	122.6	13.5	11.0
111TCP	62.9	7.8	12.3
113TCP	134.2	11.3	8.4
1B11DCP	84.7	10.8	12.7
1133TeCP	138.2	11.8	8.5
DCIM	88.3	5.7	6.4
BCIM	72.1	4.5	6.3
DBIM	69.9	7.1	10.1
CDIM	53.2	4.8	9.0
BDIM	52.0	3.3	6.3
TIM	49.2	6.4	12.9

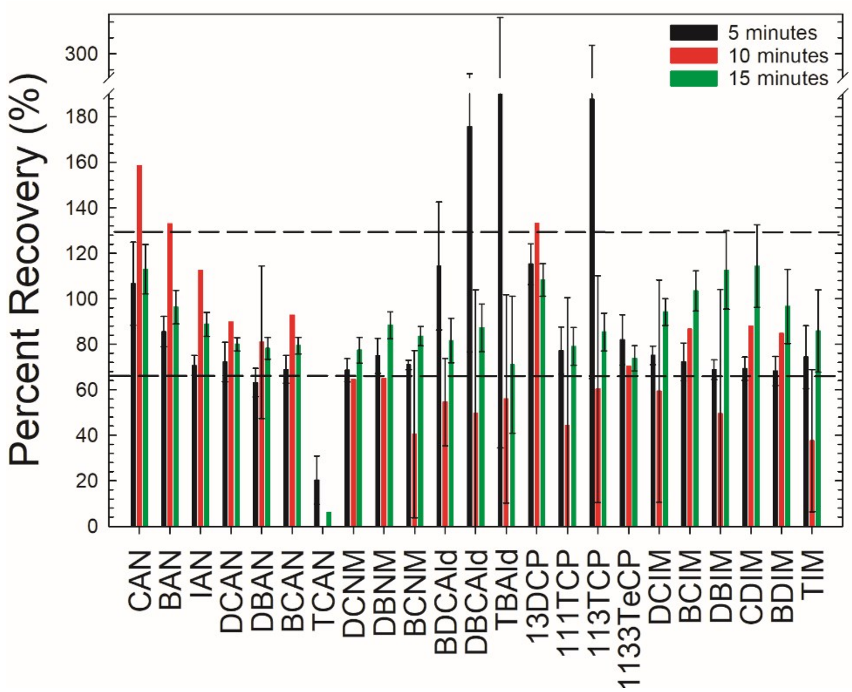

Figure S2. 5 mL x 3 MTBE was added at 5, 10, and 15 minutes shaking time. Percent recoveries for each DBP was obtained in triplicate and the average recovery was plotted in the figure. Dashed lines represent the acceptable range for DBPs (70-130%).

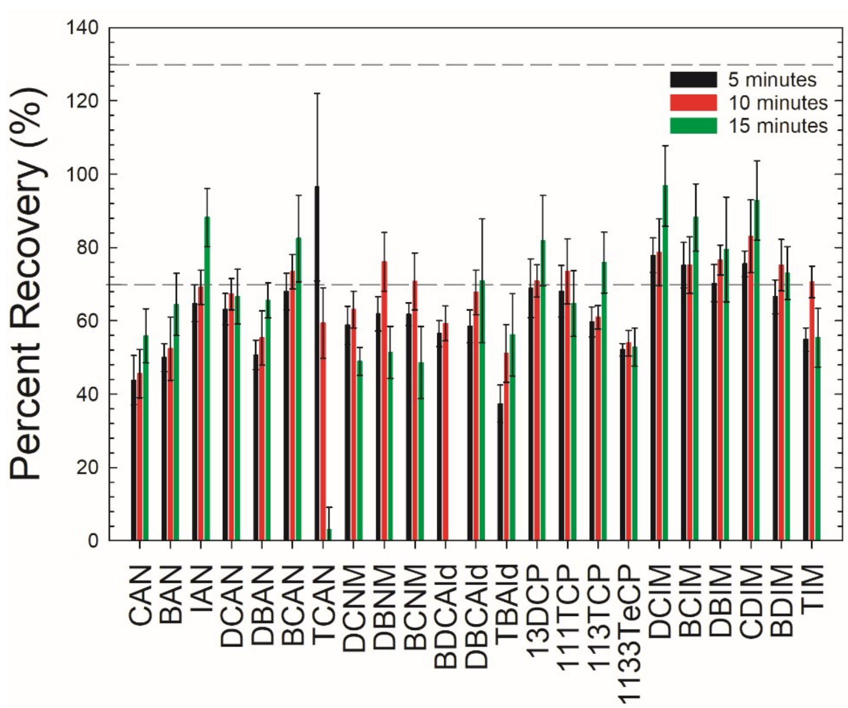

Figure S3. 1 mL x 3 MTBE was added at 5, 10, and 15 minutes shaking time. Percent recoveries for each DBP was obtained in triplicate and the average recovery was plotted in the figure. Dashed lines represent the acceptable range for DBPs (70-130%).

Table S5. Precision reported as percent relative standard deviation (RSD) of 25 DBPs using three concentrations (100 and 250 ng/L, and 100 μg/L). RSD values were calculated from n = 7 injections of the same vial into the instrument.

	RSD (%)		
DBP	100 ng/L	250 ng/L	100 μg/L
CAN	5.7	4.6	2
BAN	7	3.8	1.1
IAN	8.2	7.9	0.9
DCAN	4.6	3.6	1.4
DBAN	10.1	10.7	1.6
BCAN	8.8	5.4	2.1
TCAN	43.9	98.8	36.0
DCNM	6.5	5.4	1.5
DBNM	9.1	7.1	2.9
BCNM	8.8	8	1.1
BDCAld	< MDL	22.6	3
DBCAld	9.6	5	1.3
TBAld	10.3	10	2.6
11DCP	< MDL	4.5	3.1
13DCP	8.6	6.5	1
111TCP	10.6	9.1	1.7
113TCP	10.4	9.1	0.8
1B11DCP	7.3	7.9	1.7
1133TeCP	11.4	10.5	1.6
DCIM	6.4	6.7	2.3
BCIM	6.8	13.6	1.8
DBIM	8.2	7.9	1.1
CDIM	6.7	9.5	1.2
BDIM	9.9	10.7	1.1
TIM	8.7	8.9	1.2

Table S6. Quantified DBPs in secondary wastewater effluents (Effluent), microfiltration (UF), ozonation (UF/ozone), and reverse osmosis (UF/RO). Samples were analyzed in triplicate. Standard deviation per process was calculated as the square root of the sum of all the variances.

DBP	Effluent		UF		Ozone		RO	
	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD
CAN	n.d.		0.013	0.003	0.008	0.002	n.d.	
DCAN	0.015	0.001	0.008	0	0.090	0.002	0.005	0.001
DCNM	n.d.		0.012	0.003	n.d.		0.007	0.002
DCIM	0.013	0.001	0.012	0.004	0.014	0.003	0.010	0.003
BCIM	n.d.		n.d.		0.016	0.002	0.010	0.002
Total	0.028	0.001	0.045	0.006	0.128	0.005	0.032	0.004

Table S7. Quantified DBPs after chlorination of secondary wastewater effluents (Effluent/HOCl), microfiltration (UF/HOCl), ozonation (UF/ozone/HOCl), and reverse osmosis (UF/RO/HOCl). Samples were analyzed in triplicate. Standard deviation per process was calculated as the square root of the sum of all the variances.

DBP	Effluent/HOCl		UF/HOCl		UF/O_3/HOCl		UF/RO/HOCl	
	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD
CAN	0.40	0.04	0.44	0.02	0.16	0.00		
DCAN	12.92	0.89	13.72	0.53	5.59	0.02	0.05	0.00
TCAN	0.24	0.04	0.29	0.01	0.16	0.01		
BAN	0.18	0.02	0.18	0.01	0.09	0.01		
BCAN	2.92	0.25	2.97	0.15	1.31	0.01	0.05	0.00
DCIM	0.13	0.01	0.14	0.02	0.16	0.01	0.02	0.00
BCIM	0.02	0.00	0.03	0.00	0.02	0.00	0.01	0.01
DCNM	0.34	0.02	0.33	0.02	2.29	0.04	0.19	0.01
DBNM	n.d.		n.d.		0.19	0.00	0.04	0.00
BCNM	0.06	0.01	0.06	0.01	1.31	0.01	0.16	0.01
BDCAld	0.12	0.01	0.14	0.01	n.d.		n.d.	
DBCAld	0.24	0.01	0.24	0.01	n.d.		n.d.	
Total	17.57	0.93	18.54	0.55	11.28	0.05	0.52	0.02

Table S8. Quantified DBPs after chloramination of secondary wastewater effluents (Effluent/NH_2Cl), microfiltration (UF/ NH_2Cl), ozonation (UF/ozone/NH_2Cl), and reverse osmosis (UF/RO/NH_2Cl). Samples were analyzed in triplicate. Standard deviation per process was calculated as the square root of the sum of all the variances.

DBP	Effluent/NH_2Cl		UF/NH_2Cl		Ozone/NH_2Cl		RO/NH_2Cl	
	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD	Conc. (µg/L)	STD
DCAN	0.334	0.004	0.343	0.006	0.466	0.048	0.027	0.006
BCAN	n.d.		n.d.		0.090	0.006	n.d.	
DCNM	0.056	0.013	0.081	0.018	4.049	0.461	0.030	0.004
BCNM	n.d.		n.d.		0.200	0.021	n.d.	
11DCP	0.993	0.078	1.026	0.066	2.926	0.343	n.d.	
111TCP	n.d.		n.d.		0.046	0.006	n.d.	
DCIM	0.019	0.008	0.021	0.009	0.206	0.028	0.107	0.110
BCIM	0.009	0.005	0.010	0.003	0.016	0.002	0.020	0.002
CDIM	n.d.		n.d.		0.084	0.006	n.d.	
TIM	n.d.		n.d.		0.377	0.060	n.d.	
Total	1.411	0.080	1.481	0.069	8.460	0.581	0.184	0.110

Table S9. Comparison of method detection limits of multi-DBP analytical methods in ng/L.

DBP Class	DBP	Abb.	Weinberg et al., 2002[1]	Krasner et al., 2006[2]	Bougeard et al., 2010[3]	Carter et al., 2019[4]	Cuthbertson et al., 2020[5]	This study
HAN	Chloroacetonitrile	CAN	100	100-200		1600	100	5.7
	Bromoacetonitrile	BAN	100	100		1300	75	3.6
	Iodoacetonitrile	IAN					100	6.3
	Dichloroacetonitrile	DCAN	100	100-200	57	1600	30	3.2
	Dibromoacetonitrile	DBAN	100	100-140	41	1100	100	68.9
	Bromochloroacetonitrile	BCAN	100	100-500	70	1300	100	3.7
	Trichloroacetonitrile	TCAN	100	100-500	61	1500	40	3.2
HNM	Dichloronitromethane	DCNM	100	100-3000		1700	30	4.1
	Dibromonitromethane	DBNM	100	100	178	1100	100	2.3
	Bromochloronitromethane	BCNM	100	100		1200	100	4.1
HAL	Bromodichloroacetaldehyde	BDCAld					100	50.0
	Dibromochloroacetaldehyde	DBCAld					30	11.9
	Tribromoacetaldehyde	TBAld	100	100			100	13.0
HKT	1,1-dichloropropanone	11DCP	100	100-1000	86		100	25.7
	1,3-dichloropropanone	13DCP	100	100			100	6.8
	1,1,1-trichloropropanone	111TCP	100	100-500	286		100	30.6
	1,1,3-trichloropropanone	113TCP	100	100			30	7.5
	1-bromo-1,1-dichloropropanone	1B11DCP	100	100-3000			100	56.2
	1,1,3,3-Tetrachloropropanone	1133TeCP	100	100-500			100	5.5
I-THMs	Dichloroiodomethane	DCIM	500	100-500	257		50	5.7
	Bromochloroiodomethane	BCIM	5000	250-300	324		30	7.5
	Dibromoiodomethane	DBIM	500	250-300			100	2.0
	Chlorodiiodomethane	CDIM	100	100-500			30	3.6
	Bromodiiodomethane	BDIM	500	120-520			40	5.6
	Iodoform	TIM	2000	100-200			100	3.1

References

1. H. S. Weinberg, S. W. Krasner, S. D. Richardson and A. D. J. Thruston, *The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study*, EPA National Exposure Research Laboratory, Athens, GA, EPA/600/R-02/068, 2002.
2. S. W. Krasner, H. S. Weinberg, S. D. Richardson, S. J. Pastor, R. Chinn, M. J. Sclimenti, G. D. Onstad and A. D. Thruston Jr, Occurrence of a New Generation of Disinfection Byproducts, *Environ. Sci. Technol.*, 2006, **40**, 7175-7185.
3. C. M. M. Bougeard, E. H. Goslan, B. Jefferson and S. A. Parsons, Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine, *Water Res.*, 2010, **44**, 729-740.
4. R. A. A. Carter, D. S. Liew, N. West, A. Heitz and C. A. Joll, Simultaneous analysis of haloacetonitriles, haloacetamides and halonitromethanes in chlorinated waters by gas chromatography-mass spectrometry, *Chemosphere*, 2019, **220**, 314-323.
5. A. A. Cuthbertson, H. K. Liberatore, S. Y. Kimura, J. M. Allen, A. V. Bensussan and S. D. Richardson, Trace Analysis of 61 Emerging Br-, Cl-, and I-DBPs: New Methods to Achieve Part-Per-Trillion Quantification in Drinking Water, *Analytical Chemistry*, 2020, **92**, 3058-3068.