

Supplementary Information

for

A simultaneous detection method for eight iodinated, brominated, and chlorinated haloacetic acid disinfection byproducts in human urine: liquid-liquid extraction-acidified methanol derivatization-gas chromatography

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Table S1: Effect of sulfuric acid volume on the response strength of HAAs. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

HAA	sulfuric acid (mL)	area(mean,n=3)	area(sd)	area (%)
CAA	0	376.19	7.52	92.38
CAA	0.25	390.52	6.27	95.90
CAA	0.5	403.65	3.26	99.12
CAA	0.75	390.84	9.37	95.98
CAA	1	407.35	11.13	100.03
CAA	1.25	407.22	4.46	100.00
CAA	1.5	403.69	4.52	99.13
BAA	0	4378.72	7.84	84.13
BAA	0.25	4780.19	5.14	91.85
BAA	0.5	4968.41	3.10	95.46
BAA	0.75	4853.60	9.51	93.26
BAA	1	5096.47	10.42	97.92
BAA	1.25	5204.55	6.22	100.00
BAA	1.5	4955.75	2.67	95.22
DCAA	0	2955.27	5.71	84.13
DCAA	0.25	3226.23	5.75	91.85
DCAA	0.5	3353.27	5.65	95.46
DCAA	0.75	3275.78	11.92	93.26
DCAA	1	3439.69	4.22	97.92
DCAA	1.25	3512.64	2.17	100.00
DCAA	1.5	3344.72	12.93	95.22
TCAA	0	2426.11	3.52	18.14
TCAA	0.25	9760.78	2.23	73.00
TCAA	0.5	11524.70	11.79	86.19
TCAA	0.75	12310.60	10.28	92.07
TCAA	1	12959.80	8.19	96.93
TCAA	1.25	13370.70	12.96	100.00

TCAA	1.5	12612.30	6.97	94.33
IAA	0	893.46	5.56	6.87
IAA	0.25	10586.30	3.33	81.37
IAA	0.5	11563.10	4.90	88.88
IAA	0.75	11516.70	11.95	88.52
IAA	1	12469.00	5.96	95.84
IAA	1.25	13009.60	8.26	100.00
IAA	1.5	12560.10	9.30	96.54
BCAA	0	10068.00	6.12	58.73
BCAA	0.25	13724.50	6.34	80.06
BCAA	0.5	15583.20	5.63	90.91
BCAA	0.75	15763.40	4.30	91.96
BCAA	1	16418.60	3.90	95.78
BCAA	1.25	17141.90	9.70	100.00
BCAA	1.5	19996.40	2.35	116.65
DCBAA	0	500.95	3.11	23.23
DCBAA	0.25	1366.11	6.93	63.36
DCBAA	0.5	1655.16	3.73	76.76
DCBAA	0.75	1866.24	6.02	86.55
DCBAA	1	1992.51	7.39	92.41
DCBAA	1.25	2156.25	5.51	100.00
DCBAA	1.5	2000.00	5.41	92.75
DBAA	0	8056.66	3.81	49.06
DBAA	0.25	11845.80	5.09	72.14
DBAA	0.5	14137.30	9.74	86.10
DBAA	0.75	14478.00	9.40	88.17
DBAA	1	15628.00	2.50	95.17
DBAA	1.25	16420.40	4.71	100.00
DBAA	1.5	16567.60	2.74	100.90

Table S2: Effect of anhydrous sodium sulfate added on the response strength of HAAs. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

HAA	anhydrous sodium sulfate(g)	area(mean,n=3)	area(sd)	area(%)
CAA	0	408.14	4.50	80.40
CAA	1	428.78	2.66	84.46
CAA	2	447.89	9.39	88.23
CAA	3	472.24	9.83	93.02
CAA	4	507.65	2.67	100.00
CAA	5	484.81	6.61	95.50
CAA	6	495.65	6.21	97.64
BAA	0	5248.38	6.55	82.82
BAA	1	5576.47	5.02	88.00
BAA	2	5703.35	7.57	90.00
BAA	3	5913.23	10.10	93.31
BAA	4	6336.89	6.08	100.00
BAA	5	6051.21	10.86	95.49
BAA	6	6141.79	3.33	96.92
DCAA	0	4862.92	3.26	129.48
DCAA	1	4251.38	8.55	113.19
DCAA	2	4000.67	4.30	106.52
DCAA	3	3713.92	6.04	98.88
DCAA	4	3755.82	7.28	100.00
DCAA	5	3355.58	3.51	89.34
DCAA	6	3386.27	6.59	90.16
TCAA	0	13421.90	7.40	89.13
TCAA	1	13589.90	6.10	90.24
TCAA	2	13607.10	5.41	90.36
TCAA	3	13926.20	7.67	92.48
TCAA	4	15059.40	10.21	100.00
TCAA	5	14401.80	8.59	95.63

TCAA	6	14832.60	6.07	98.49
IAA	0	13117.40	4.30	85.30
IAA	1	13747.50	5.88	89.40
IAA	2	13802.00	10.47	89.75
IAA	3	14293.10	9.58	92.95
IAA	4	15377.70	8.30	100.00
IAA	5	14754.30	2.68	95.95
IAA	6	14994.90	9.62	97.51
BCAA	0	20144.00	2.85	106.00
BCAA	1	17775.80	3.11	93.54
BCAA	2	17605.10	9.03	92.64
BCAA	3	18122.10	9.25	95.36
BCAA	4	19004.30	9.79	100.00
BCAA	5	18010.50	2.56	94.77
BCAA	6	18414.40	7.34	96.90
DCBAA	0	853.16	2.14	34.62
DCBAA	1	1945.48	5.63	78.94
DCBAA	2	2025.43	9.12	82.18
DCBAA	3	2152.17	9.70	87.33
DCBAA	4	2464.55	4.26	100.00
DCBAA	5	2438.78	2.17	98.95
DCBAA	6	2522.82	3.67	102.36
DBAA	0	17607.30	9.20	96.26
DBAA	1	16908.00	7.29	92.43
DBAA	2	16743.40	8.05	91.53
DBAA	3	17086.30	2.08	93.41
DBAA	4	18292.00	6.36	100.00
DBAA	5	17205.60	9.53	94.06
DBAA	6	17655.70	9.56	96.52

Table S3: Effect of A/M on the response strength of HAAs. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

HAA	A/M	area(mean,n=3)	area(sd)	area(%)
CAA	1	864.15	5.92	100.00
CAA	1.5	787.47	3.44	91.13
CAA	2	776.79	2.90	89.89
CAA	2.5	891.44	10.97	103.16
CAA	3	802.30	2.55	92.84
CAA	3.5	910.40	2.74	105.35
BAA	1	10234.00	9.68	100.00
BAA	1.5	9796.31	8.50	95.72
BAA	2	10024.60	5.89	97.95
BAA	2.5	12546.88	11.90	122.60
BAA	3	12997.18	9.46	127.00
BAA	3.5	13191.63	7.73	128.90
DCAA	1	8561.65	7.44	100.00
DCAA	1.5	9658.70	3.70	112.81
DCAA	2	12279.60	5.23	143.43
DCAA	2.5	13998.30	9.85	163.50
DCAA	3	15213.20	12.75	177.69
DCAA	3.5	15649.84	4.96	182.79
TCAA	1	24824.70	6.34	100.00
TCAA	1.5	28327.00	11.50	114.11
TCAA	2	36465.40	11.94	146.89
TCAA	2.5	60671.57	5.60	244.40
TCAA	3	70477.32	4.75	283.90
TCAA	3.5	75988.41	6.39	306.10
BCAA	1	28942.50	3.42	100.00
BCAA	1.5	28917.06	3.29	99.91
BCAA	2	31277.11	11.14	108.07

BCAA	2.5	41803.21	5.78	144.44
BCAA	3	49195.21	5.45	169.98
BCAA	3.5	53994.74	3.41	186.56
IAA	1	24121.10	7.15	100.00
IAA	1.5	25133.62	12.88	104.20
IAA	2	34387.18	6.67	142.56
IAA	2.5	45371.17	11.06	188.10
IAA	3	55005.36	12.93	228.04
IAA	3.5	62506.09	2.93	259.13
DCBAA	1	3717.02	2.95	100.00
DCBAA	1.5	4903.27	7.72	131.91
DCBAA	2	5557.26	10.74	149.51
DCBAA	2.5	15054.30	9.79	405.01
DCBAA	3	16499.85	11.68	443.90
DCBAA	3.5	16899.80	8.36	454.66
DBAA	1	28594.90	8.69	100.00
DBAA	1.5	30810.70	11.82	107.75
DBAA	2	40640.90	5.20	142.13
DBAA	2.5	60170.60	12.80	210.42
DBAA	3	68999.49	7.16	241.30
DBAA	3.5	69997.46	7.58	244.79

Table S4: Effect of derivatization time on the response strength of HAAs. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

HAA	time(h)	area(mean,n=3)	area(sd)	area(%)
CAA	0	575.63	3.25	87.81
CAA	0.5	619.84	2.38	94.55
CAA	1	624.12	4.54	95.20
CAA	1.5	637.73	8.46	97.28
CAA	2	655.56	9.56	100.00
CAA	2.5	653.28	7.12	99.65
BAA	0	5956.31	5.30	101.85
BAA	0.5	5786.77	5.58	98.95
BAA	1	5641.20	9.76	96.46
BAA	1.5	5794.46	2.38	99.08
BAA	2	5848.06	5.62	100.00
BAA	2.5	5867.70	2.65	100.34
DCAA	0	3968.14	4.46	97.00
DCAA	0.5	3977.00	5.63	97.22
DCAA	1	3967.53	6.30	96.99
DCAA	1.5	4051.34	8.03	99.03
DCAA	2	4090.83	8.96	100.00
DCAA	2.5	4088.06	2.70	99.93
TCAA	0	15135.68	11.89	96.73
TCAA	0.5	15416.47	4.83	98.53
TCAA	1	15257.21	11.86	97.51
TCAA	1.5	15239.46	6.74	97.39
TCAA	2	15647.10	4.90	100.00
TCAA	2.5	15586.76	2.04	99.61
BCAA	0	10274.63	3.63	70.53
BCAA	0.5	13609.68	9.60	93.42
BCAA	1	14050.09	10.31	96.44

BCAA	1.5	14198.58	8.47	97.46
BCAA	2	14568.00	10.90	100.00
BCAA	2.5	14646.79	9.85	100.54
IAA	0	7121.51	8.63	56.62
IAA	0.5	12247.73	10.31	97.37
IAA	1	12142.01	8.89	96.53
IAA	1.5	12365.19	9.46	98.30
IAA	2	12578.60	10.61	100.00
IAA	2.5	12541.70	5.71	99.71
DCBAA	0	2061.39	4.27	67.86
DCBAA	0.5	2695.92	5.28	88.74
DCBAA	1	2743.27	8.75	90.30
DCBAA	1.5	2759.61	5.49	90.84
DCBAA	2	3037.87	7.63	100.00
DCBAA	2.5	3074.23	6.02	101.20
DBAA	0	15193.70	10.69	80.54
DBAA	0.5	18138.69	2.48	96.15
DBAA	1	18276.91	3.63	96.89
DBAA	1.5	18303.02	2.70	97.02
DBAA	2	18864.30	2.57	100.00
DBAA	2.5	18880.45	7.25	100.09

Table S5: Effect of sodium sulfate solution added on the response strength of HAAs. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

HAA	sodium sulfate solution(mL)	area(mean,n=3)	sd	area(%)
CAA	6	946.35	4.06	100.00
CAA	7	943.58	6.90	99.71
CAA	8	887.92	3.90	93.83
CAA	9	837.86	7.90	88.54
CAA	10	851.87	9.29	90.02
BAA	6	9870.53	5.02	100.00
BAA	7	9810.84	9.61	99.40
BAA	8	9750.81	2.79	98.79
BAA	9	9716.73	4.15	98.44
BAA	10	9645.17	5.23	97.72
DCAA	6	9037.51	8.99	100.00
DCAA	7	9033.09	4.25	99.95
DCAA	8	8649.26	4.85	95.70
DCAA	9	8637.17	11.48	95.57
DCAA	10	8494.76	6.49	93.99
TCAA	6	25884.90	8.30	100.00
TCAA	7	25810.61	9.32	99.71
TCAA	8	25747.00	3.28	99.47
TCAA	9	25053.19	2.80	96.79
TCAA	10	24535.38	10.41	94.79
BCAA	6	34270.40	8.28	100.00
BCAA	7	34039.96	8.74	99.33
BCAA	8	32038.71	11.57	93.49
BCAA	9	29950.54	9.89	87.39
BCAA	10	27440.44	7.55	80.07
IAA	6	23604.40	9.79	100.00
IAA	7	23244.18	4.60	98.47

IAA	8	23162.35	8.83	98.13
IAA	9	23032.36	3.62	97.58
IAA	10	21864.76	6.50	92.63
DCBAA	6	3872.54	6.99	100.00
DCBAA	7	3452.88	9.55	89.16
DCBAA	8	3288.51	6.59	84.92
DCBAA	9	3098.35	9.50	80.01
DCBAA	10	2801.00	10.80	72.33
DBAA	6	30454.20	5.27	100.00
DBAA	7	30793.95	9.07	101.12
DBAA	8	28216.92	2.15	92.65
DBAA	9	27650.16	11.19	90.79
DBAA	10	26631.63	5.11	87.45

Table S6: Effect of the influence of sodium sulfate solution volume and A/M on the volume of MTBE recovered. The concentration of HAAs was 20 µg/L (mean ± SD, n = 3)

A/M	sodium sulfate solution(mL)	MTBE volumn (estimated value)
1	5	1900
1	6	1900
1	7	1850
1	8	1870
1	9	1900
1	10	1800
1.5	5	1500
1.5	6	1600
1.5	7	1650
1.5	8	1660
1.5	9	1660

1.5	10	1670
2	5	700
2	6	1050
2	7	1020
2	8	1000
2	9	1050
2	10	1000
2.5	5	200
2.5	6	450
2.5	7	800
2.5	8	830
2.5	9	850
2.5	10	860
3	5	0
3	6	0
3	7	0
3	8	250
3	9	350
3	10	380
3.5	5	0
3.5	6	0
3.5	7	0
3.5	8	0
3.5	9	200
3.5	10	350

Table S7 Concentrations of HAAs (µg/L) in urine samples (N=460)

Chemicals	Detection frequency (%)	Concentrations (µg/L)					
		Min	P ₂₅	P ₅₀	P ₇₅	Max	GM ^a
CAA	94.7	<MDL ^b	0.49	0.61	0.76	14.95	0.59
DCAA	85.7	<MDL	0.09	0.49	0.90	22.45	0.30
TCAA	99.3	<MDL	0.48	0.86	1.59	42.31	0.89
IAA	91.6	<MDL	0.04	0.07	0.11	6.20	0.07
BCAA	4.2	<MDL	<MDL	<MDL	<MDL	5.31	\ ^c
DBAA	95.8	<MDL	0.41	0.45	0.53	15.28	0.43
ΣHAAs		0.57	2.02	2.67	4.30	43.33	3.09

^a: GM represents the geometric mean of each target analyte.

^b: Below the method, the detection limit was defined as not detected and was not included in the calculation of the detection frequency. Values below the method detection limit were used in the statistical calculation at 1/2 the detection limit.

^c: The detection frequency was lower than 50%, and GM was not calculated.