

Trace Level Haloacetic Acids in Drinking Water by Direct Injection Ion Chromatography and Single Quadrupole Mass Spectrometry*

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Abstract

Chlorine has been widely used to kill disease-causing microbes in drinking water. During the disinfection process, organic and inorganic material in source waters can combine with chlorine and certain other chemical disinfectants to form disinfection by-products. The kind of disinfectant used can produce different types and levels of disinfectant byproducts in the drinking water, such as trihalomethanes and haloacetic acids (5HAAs). Currently, USEPA Method 552 utilizes a methyl tert-butyl ether extraction and diazomethane derivatization of HAAs and phenolic disinfectant by-products, and a gas chromatograph equipped with a capillary column to perform the separation of methyl-haloacetates and anisoles. To detect, gas chromatography and electron capture detector are used. This article demonstrates a simple method using direct injection ion chromatography hyphenated with mass spectrometry for the analysis of 5HAAs.

Introduction

Chlorine has been widely used to kill disease-causing microbes in drinking water. The addition of chlorine in public water systems across the U.S. to kill microbial pathogens in the water supply has been cited as one of the greatest public health advances of the twentieth century (1). For example, during the decade 1880–1890, American cities experienced an average mortality rate of 58 per 100,000 from typhoid, which was commonly transmitted through contaminated water. By 1938, this rate had fallen to 0.67 deaths per 100,000, largely due to improved treatment of drinking water (2).

During the disinfection process, organic and inorganic material in source waters can combine with chlorine and certain other chemical disinfectants to form disinfection by-products (DBPs). More than 260 million people in the U.S. are exposed to disinfected water and DBPs (3). Although chlorine is the most commonly applied disinfectant, other disinfectants, including ozone, chlorine dioxide, chloramine, and UV radiation, are in use. In combination with these, all surface water systems must also use either chlorine or chloramine to maintain a disinfectant residual in their distribution system. The kind of disinfectant used can produce different types and levels of disinfectant by-products in the drinking water.

Tri-halo methanes (THMs) and haloacetic acids (HAAs) are widely occurring classes of DBPs formed during disinfection with chlorine and chloramine. The four THMs (TTHM) and five HAAs (HAA5) measured and regulated in the Stage 2 DBPR act as indicators for DBP occurrence. There are other known DBPs in addition to a variety of unidentified DBPs present in disinfected water. THMs and HAAs typically occur at higher levels than other known and unidentified DBPs (4,5). The presence of TTHM and HAA5 is representative of the occurrence of many other chlorination DBPs; thus, a reduction in the TTHM and HAA5 generally indicates an overall reduction of DBPs. TTHM and HAA5 in excess causes “fouled” taste of water; in addition, they are potential carcinogens.

Instrumental and Operating Conditions

The analytical system consists of an MIC-2 advanced ion chromatograph (IC) with a front-end in-line sample preparation module (Metrohm-Peak, Inc., Houston, TX) and an 1100 MSD SL Quad (Agilent Technologies, Palo Alto, CA). A standard electro-spray interface was used. The system was synchronized by use of a software patch on an Agilent Chemstation ver. B.02 software package and remote contact closure

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between the IC and the mass spectrometer (MS). A complete list of instrumental parameters is listed in the following. Metrohm Advanced IC; column set: Metrosep ASUPP1 + Metrosep ASUPP5 (4 mm i.d. × 150 mm); eluent: 3.2 mM sodium carbonate + 1.0 mM sodium hydrogen carbonate; suppressor regenerant solution: 100 mM nitric acid + 2.0 mM oxalic acid; suppressor rinse solution: 18 meg Ω UHP deionized water; 100 μL loop injection; Agilent 1100 LC–MSD ESI; negative mode “auto-tune”; $V_{cap} = 2000$ V, drying gas = 12.5 L/min @ 350°C (Dominick-Hunter N₂ generator model# LCMS20 was used to provide 99.5% pure nitrogen); nebulizer pressure = 40 psig;

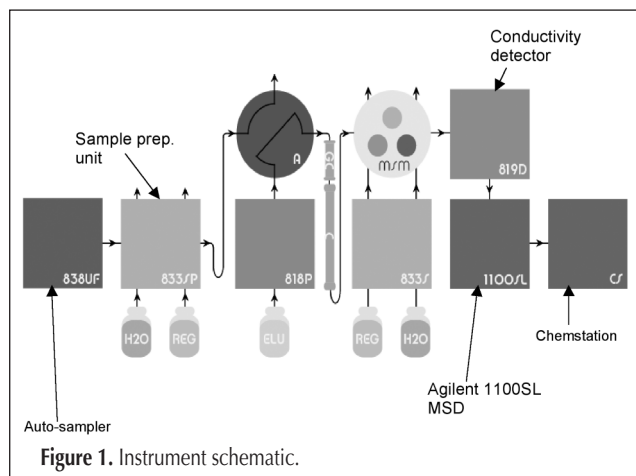


Figure 1. Instrument schematic.

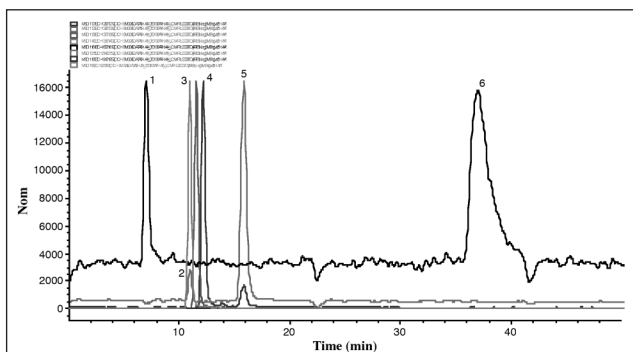


Figure 2. Extracted ion chromatogram for calibration standard. Peaks: 1, MChIAA; 2, bromate; 3, MBrAA and MBrAA (ISTD); 4, dichloroacetic acid (DiChIAA); 5, dibromoacetic acid (DiBrAA); 6, trichloroacetic acid (TriChIAA).

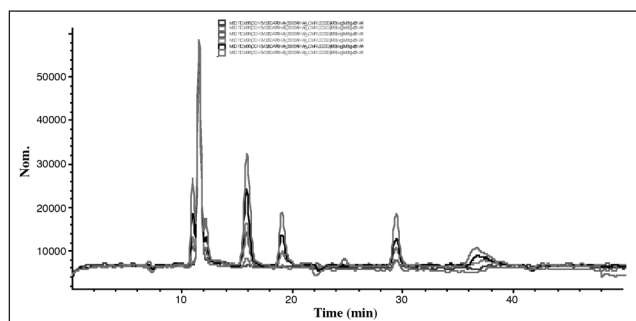


Figure 3. Stacked total ion chromatograms for blank + calibration standards.

fragmentor voltage = variable (optimized for each analyte); flow rate: 0.7 mL/min with no matrix diversion and matrix splitting). These conditions are used for all the figures. Please refer to Figure 1 for system configuration.

Method optimization for mass spectrometer

The fast injection analysis feature of Agilent Chemstation software was employed for method optimization. Every two min, 100 μL of each analyte was injected into the MS for optimizing each parameter (fragmentor voltage, capillary voltage, nebulizer pressure, drying gas temperature, and flow, etc.).

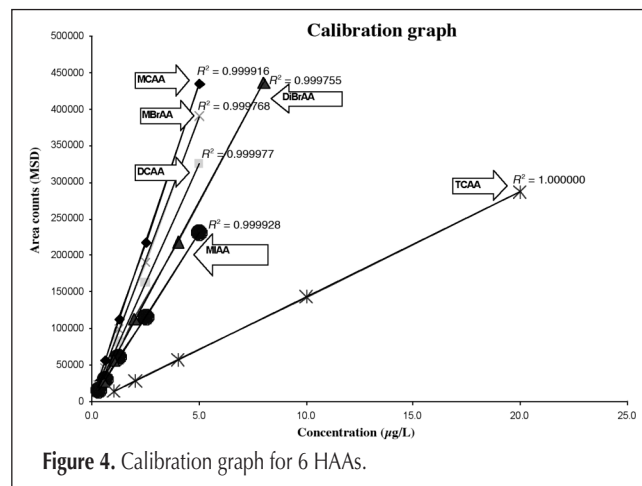


Figure 4. Calibration graph for 6 HAAs.

Table I. Calibration Standards with Internal Standard

Component	Concentration (μg/L)				
	Level 1	Level 2	Level 3	Level 4	Level 5
MChIAA	0.30	0.60	1.30	2.50	5.00
Bromate	0.30	0.60	1.30	2.50	5.00
MBrAA	0.30	0.60	1.30	2.50	5.00
MBrAA (ISTD)	5.00	5.00	5.00	5.00	5.00
MIAA	0.30	0.60	1.30	2.50	5.00
DiChIAA	0.30	0.60	1.30	2.50	5.00
DiBrAA	0.50	1.00	2.00	4.00	8.00
TriChIAA	1.00	2.00	4.00	10.00	20.00

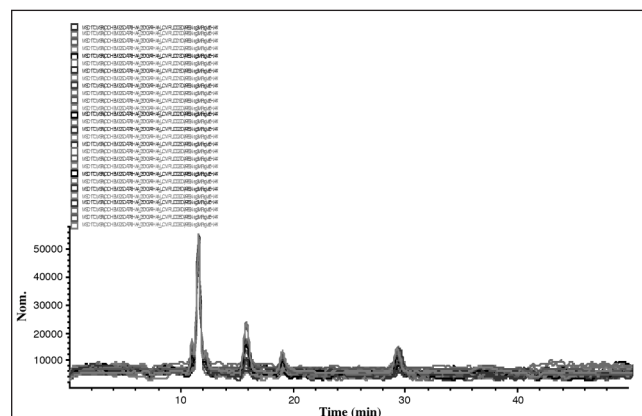


Figure 5. Stacked chromatograms for LCMRL study.

After optimizing each analyte, a mixture of 100 parts-per-billion (ppb) and 10 ppb was analyzed to further optimize the effects of MS fragmentation in the sample matrix.

Standard and sample preparation

All standards and samples were prepared according to US EPA Method 552.3.

Two grams per liter of ammonium chloride was added as a preservative to capture and free chlorine gas in the sample to form chloramines.

All the samples were analyzed using the ultra-filtration feature of the Metrohm Autosampler (model 838), and then passed through in-line sample preparation module (model 833 SPP) to stabilize the pH of the sample; it also removes divalent cations (total hardness as calcium and magnesium) and transition metals (like Fe^{+3} , Al^{+3} , Ni^{+2} , etc.) from the sample, and this enhances the chromatography and extends the life of the guard + analytical column set.

Results and Discussion

Sample information

The pH, total hardness [as $\text{Ca}(\text{CO}_3)_2$], and total organic carbon (TOC) can affect the results of the HAAs. TOC values for these samples varied from 4–10 parts-per-million (ppm); total hardness [as $\text{Ca}(\text{CO}_3)_2$] varied from 50 ppm to 275 ppm. The pH of the samples provided from the water utility company varied from 7.1 to 8.9. Variation in pH of the sample along with the presence of metal ions (total hardness, transition metals) may cause analytical challenges for ion-exchange columns and suppressor. To overcome variability of pH and hardness, the use of an in-line sample preparation module (model 833 SPP) helped tremendously by stabilizing the pH and removing interfering cations before the injection loop. Figure 2 demonstrates the separation of each component.

Calibration

Figure 3 demonstrates a stacked total ion chromatogram for calibration standards and Figure 4 demonstrates the linear calibration for each analyte. Refer to Table I for the analyte and its concentration information.

^{13}C labeled mono bromo acetic acid. ^{13}C labeled mono bromo acetic acid [MBrAA (ISTD)] was used as an internal standard. This compound was commercially purchased from Sigma-Aldrich Corporation (St. Louis, MO).

Method detection limit study

Table II demonstrates the method detection limit (MDL) study. MDL is calculated using the

Table II. MDL Study*

Analysis number	Concentration (ppb)							
	MChIAA	Bromate	MBrAA	MBrAA (ISTD)	MIAA	DiChIAA	DiBrAA	TriChIAA
1	0.25	0.109	0.250	5.00	0.250	0.200	0.250	0.750
2	0.249	0.101	0.255	5.00	0.249	0.199	0.248	0.749
3	0.234	0.099	0.260	5.00	0.250	0.189	0.244	0.755
4	0.251	0.098	0.245	5.00	0.248	0.199	0.249	0.756
5	0.245	0.102	0.250	5.00	0.249	0.203	0.255	0.751
6	0.256	0.103	0.246	5.00	0.255	0.200	0.251	0.749
7	0.249	0.095	0.239	5.00	0.239	0.201	0.235	0.751
Average	0.248	0.101	0.249	5.000	0.249	0.199	0.247	0.752
Standard deviation	0.00687	0.00443	0.00687		0.00479	0.00450	0.00640	0.00282
MDL (calculated)	0.02158	0.01392	0.02158		0.01504	0.01413	0.02009	0.00885
RSD%	2.775%	4.391%	2.757%		1.927%	2.264%	2.586%	0.375%

* MDL calculated = 3.14 (t-95 student value) × standard deviation.

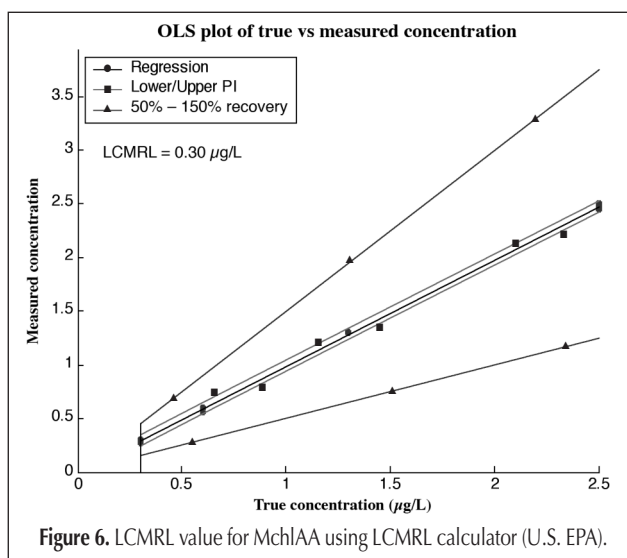


Table III. Various "Real World" Sample Data

Sample ID	Component concentration (µg/L)							
	MChIAA	Bromate	MBrAA	MBrAA (ISTD)	MIAA	DiChIAA	DiBrAA	TriChIAA
Houston City tap water	0.000	0.369	0.000	4.90	0.000	0.346	0.000	0.870
Pearland City tap water	0.000	0.109	0.000	4.94	0.000	0.350	0.000	0.884
College Station tap water	0.000	0.000	0.000	5.01	0.000	0.341	0.000	0.875
LWS Station-1 water	1.492	0.891	0.000	4.88	0.000	7.895	0.569	5.723
LWS DS-2 water	1.591	0.782	0.000	4.93	0.000	6.387	0.601	6.329
LWS Station-2 water	1.234	0.798	0.000	4.98	0.000	6.892	0.478	7.012
LWS T-1 water	1.198	0.654	0.000	4.79	0.000	5.459	0.698	4.598
LWS T-2 water	1.209	0.569	0.000	4.78	0.000	6.138	0.663	5.520

following formula:

MDL = standard deviation of concentration (seven replicates)
 $\times 3.14$ (t-95 student value).

Lowest concentration minimum reporting limit study

This is a new concept from the US EPA of studying MDL and minimum reporting limits (MRLs) at the same time. Figure 5 is a representation of stacked chromatograms for the lowest concentration (LC) MRL study. These replicates indicate the excellent stability and robustness of the application. Figure 6 is a graph explaining an example of LCMRL for monochloroacetic acid (MChIAA). Similar calculations were performed individually for all the analytes.

Sample ID	Component concentration ($\mu\text{g/L}$)							
	MChIAA	Bromate	MBrAA	MBrAA (ISTD)	MIAA	DiChIAA	DiBrAA	TriChIAA
Houston City tap water-1	0.000	0.369	0.000	4.82	0.000	0.346	0.000	0.870
Houston City tap water-2	0.000	0.381	0.000	4.86	0.000	0.350	0.000	0.884
Houston City tap water-3	0.000	0.379	0.000	4.90	0.000	0.341	0.000	0.875
Houston City tap water-spike-1	2.456	3.012	2.476	4.93	2.389	2.819	2.474	3.255
Houston City tap water-spike-2	2.442	3.039	2.489	4.97	2.421	2.783	2.501	3.259
Houston City tap water-spike-3	2.457	2.934	2.561	5.01	2.439	2.821	2.486	3.265
Avg. Houston City tap water	0.000	0.376	0.000		0.000	0.346	0.000	0.876
Avg. Houston City tap water spike	2.452	2.995	2.509		2.416	2.808	2.487	3.260
True spike value	2.500	2.500	2.500		2.500	2.500	2.500	2.500
Spike recovery	98.07%	104.75%	100.35%		96.65%	98.48%	99.48%	95.33%

Real world samples from a Midwestern water utility company in the U.S.

One of the Metrohm-Peak LLC's customers was gracious enough to provide samples for this project. This water utility uses the chloramination disinfectant process for drinking water. Local tap water from Houston, Texas was analyzed as well. Houston City water is a blend of surface- and groundwater in the ratio of 45:55 percent.

Table III demonstrates the data for each matrix and analytes, and Table IV represents spike recovery data for "real world" samples.

Conclusion

Currently, 5 HAAs are regulated by the U.S. EPA. The analytical method used is US EPA 552.3. The current method uses liquid-liquid extraction as a sample preparation method prior to gas chromatography-electron capture detection analysis. According to this paper, it is evident that IC hyphenated with MS is a much simpler method because it injects water samples directly into the instrument without any sample preparation steps. Metrohm in-line sample preparation (MISP) also permits pH stabilization for the matrix containing free chlorine. Figure 6 (LCMRL graph for MChIAA) and Table V (extended statistics for LCMRL) clearly indicate that data produced by the instrument matches the theoretical values of detection limits. The LCMRL concept is more robust and rugged when compared to a traditional MDL study (it saves time for the analyst in longer run). Figure 5 (stacked chromatogram for LCMRL Table VI) indicates the stability, ruggedness, and robustness of the entire application including the instrument. Each analysis time is ~ 45 min, and the instrument was subjected to run more than 79 samples (continuous operation of 59.25 h); even after so many samples, there was no evident of instrument performance degradation. This successful performance of the system is

Sample ID	Component concentration ($\mu\text{g/L}$)							
	MChIAA	Bromate	MBrAA	MBrAA (ISTD)	MIAA	DiChIAA	DiBrAA	TriChIAA
Avg. LCMRL-1 ($n = 7$)	0.293	0.292	0.287	4.963	0.302	0.288	0.484	0.952
SD LCMRL-1 ($n = 7$)	0.012	0.003	0.006	0.052	0.023	0.012	0.005	0.017
RSD %	4.185	1.068	2.157	1.050	7.546	4.075	0.961	1.762
Avg. LCMRL-2 ($n = 7$)	0.593	0.597	0.599	4.960	0.593	0.598	1.002	1.978
SD LCMRL-2 ($n = 7$)	0.018	0.009	0.007	0.083	0.009	0.007	0.011	0.044
RSD %	3.007	1.459	1.182	1.667	1.474	1.140	1.080	2.221
Avg. LCMRL-3 ($n = 7$)	1.304	1.300	1.306	4.987	1.302	1.294	2.043	4.043
SD LCMRL-3 ($n = 7$)	0.005	0.007	0.009	0.053	0.002	0.008	0.047	0.040
RSD %	0.358	0.560	0.662	1.067	0.187	0.599	2.296	0.997
Avg. LCMRL-4 ($n = 7$)	2.468	2.492	2.515	4.929	2.492	2.485	3.976	9.956
SD LCMRL-4 ($n = 7$)	0.025	0.014	0.035	0.010	0.094	0.018	0.101	0.045
RSD %	1.022	0.565	1.393	0.198	3.780	0.733	2.541	0.455
LCMRL value	0.330	0.182	0.313	N/A	0.288	0.100	0.368	0.329

Table VI. LCMRL Study

Sample ID	Component concentration (µg/L)							
	MChIAA	Bromate	MBrAA	MBrAA (ISTD)	MIAA	DiChIAA	DiBrAA	TriChIAA
Blank	0.000	0.000	0.000	4.98	0.000	0.000	0.000	0.000
CCC (Cal-1)	0.278	0.301	0.313	4.88	0.298	0.278	0.487	0.908
LCMRL-1-1	0.296	0.289	0.291	4.95	0.290	0.289	0.480	0.920
LCMRL-1-2	0.301	0.291	0.281	4.96	0.283	0.287	0.492	0.960
LCMRL-1-3	0.309	0.290	0.281	4.89	0.279	0.305	0.486	0.940
LCMRL-1-4	0.300	0.290	0.280	4.92	0.289	0.301	0.478	0.960
LCMRL-1-5	0.291	0.294	0.289	4.97	0.310	0.287	0.485	0.952
LCMRL-1-6	0.282	0.295	0.291	5.01	0.324	0.280	0.482	0.963
LCMRL-1-7	0.273	0.297	0.295	5.05	0.339	0.271	0.482	0.969
Blank	0.000	0.000	0.000	4.76	0.000	0.000	0.000	0.000
CCC (Cal-3)	1.298	1.301	1.310	4.88	1.278	1.298	1.923	3.890
LCMRL-2-1	0.556	0.607	0.601	5.01	0.578	0.604	1.020	1.970
LCMRL-2-2	0.589	0.603	0.599	4.98	0.589	0.602	0.993	1.923
LCMRL-2-3	0.592	0.600	0.592	4.79	0.601	0.591	0.994	1.926
LCMRL-2-4	0.601	0.581	0.589	4.98	0.590	0.601	0.997	1.970
LCMRL-2-5	0.605	0.591	0.599	5.02	0.592	0.602	0.992	2.011
LCMRL-2-6	0.598	0.601	0.601	5.02	0.601	0.601	1.012	2.001
LCMRL-2-7	0.610	0.599	0.611	4.92	0.602	0.586	1.005	2.042
Blank	0.000	0.000	0.000	4.92	0.000	0.000	0.000	0.000
CCC (Cal-1)	0.279	0.289	0.301	4.67	0.299	0.284	0.489	0.918
LCMRL-3-1	1.310	1.304	1.309	4.99	1.304	1.298	2.100	4.090
LCMRL-3-2	1.299	1.289	1.292	5.01	1.300	1.279	2.092	4.052
LCMRL-3-3	1.302	1.294	1.305	5.05	1.301	1.296	2.082	4.020
LCMRL-3-4	1.305	1.304	1.310	5.00	1.302	1.289	1.993	3.996
LCMRL-3-5	1.302	1.297	1.299	4.97	1.301	1.292	2.003	4.040
LCMRL-3-6	1.310	1.311	1.319	4.88	1.307	1.302	2.030	4.098
LCMRL-3-7	1.299	1.301	1.309	5.01	1.301	1.299	2.001	4.002
Blank	0.000	0.000	0.000	5.02	0.000	0.000	0.000	0.000
CCC (Cal-3)	1.310	1.295	1.273	4.95	1.302	1.306	1.889	3.930
LCMRL-4-1	2.449	2.468	2.590	4.92	2.645	2.449	4.102	10.020
LCMRL-4-2	2.509	2.510	2.492	4.94	2.561	2.501	4.091	10.002
LCMRL-4-3	2.492	2.503	2.499	4.94	2.491	2.495	4.030	9.976
LCMRL-4-4	2.475	2.496	2.506	4.93	2.421	2.489	3.969	9.950
LCMRL-4-5	2.458	2.489	2.513	4.93	2.351	2.483	3.908	9.924
LCMRL-4-6	2.441	2.482	2.520	4.92	2.481	2.477	3.847	9.898
LCMRL-4-7	2.450	2.498	2.486	4.92	2.491	2.501	3.887	9.920
Blank	0.000	0.000	0.000	4.91	0.000	0.000	0.000	0.000
CCC (Cal-1)	0.289	0.278	2.801	4.91	0.279	0.280	0.480	0.906

mainly due to the MISP module. MISP allows stabilization the sample matrix prior to introduction in the IC system. We have noticed and documented that IC-MS is a better choice for the analysis of HAAs in drinking water.

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