

Application News

No. GC-2001

Gas Chromatography

Determination of Haloacetic Acids (HAA5 and HAA9) in Drinking Water According to EPA Method 552.3

■ Abstract

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently, five HAAs are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) and occurrence of four more HAAs is being monitored under the Unregulated Contaminant Rule 4 (2018-2020)¹. EPA method 552.3² is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon. This publication demonstrates the performance of the Shimadzu Nexis GC-2030 with dual ECD, equipped with ClickTek technology, for the analysis of the ten target compounds included in EPA method 552.3 using helium as carrier gas. Precision was under 11% and accuracy ranged between 78-110% of expected values, meeting and exceeding the quality assurance criteria outlined in EPA method 552.3.

■ Introduction

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently five HAAs are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) and a Maximum Contaminant Level of 60 ppb for the sum of these five compounds (MCAA, MBAA, DCAA, TCAA, DBAA). The occurrence of four more HAAs (BCAA, BDCAA, CDBAA, TBAA) is being assessed under the Unregulated Contaminant Rule 4 (UCMR4). HAA5 are regularly monitored by water utilities to comply with federal regulations.

Requirements for the analysis of HAA9 beyond the scope of UCMR4 will be determined once the rule is completed; however, some utilities already monitor them as means of process control during water treatment. EPA method 552.3 is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon¹.

Table 1: List of HAAs included in EPA 552.3

Compound	Acronyms	HAA Group	
Monochloroacetic acid	MCAA	HAA5	HAA9
Monobromoacetic acid	MBAA		
Dichloroacetic acid	DCAA		
Trichloroacetic acid	TCAA		
Dibromoacetic acid	DBAA		
Bromochloroacetic acid	BCAA		
Bromodichloroacetic acid	BDCAA		
Chlorodibromoacetic acid	CDBAA		
Tribromoacetic acid	TBAA		

In this application, HAA5 and HAA9 were analyzed according to EPA method 552.3 using a Shimadzu Nexis GC-2030 with an ECD detector. EPA method 552.3 requires the confirmation of analytes identification by analyzing the samples in two dissimilar columns (ex. Rtx-1701 and Rxi5Sil-MS). To achieve the throughput required in modern laboratories the GC-2030 was equipped with dual injectors, ECD detectors and autosamplers. With this configuration, the EPA's requirements for identification, quantification and confirmation of HAAs and dalapon can be completed in one GC run. Advanced features of the GC-2030, such as a gas saver function, automatic startup and shutdown (available through LabSolutions software), minimize gas consumption, and hence, reduce operational cost and environmental impact. This is particularly relevant nowadays due to the depletion of the global helium supply.

■ Materials and Methods

Reagents

ECD grade tert-butyl methyl ester (MTBE) was purchased from Sigma (Cat. No. 1019951000). Haloacetic Acid Methyl Ester Mix #1 (6 components, Cat. No. 31645) and internal standard (IS) solution (1,2,3-trichloropropane, Cat. No. 31648) were purchased from Restek. Haloacetic Acid Methyl Ester Mix #2 (11 components, Cat. No. M-552.3) mix was purchased from Accustandards. Each methylated standard mix was diluted in MTBE with 1ppm internal standard to indicated concentrations.

Instrumentation

A Shimadzu GC-2030 with dual line split/splitless injector, dual ECD Exceed detector and dual autosampler was used for analysis of HAA5, HAA9 and dalapon according to EPA method 552.3 using helium as carrier gas. Methylated form of HAAs, Dalapon and surrogate as well as the internal standard were analyzed on the GC system. Analysis conditions are outlined in Table 2. LabSolutions software was used for data acquisition and processing. Concentrations reported in section "Results and Discussion" represent the concentration in the water samples, before extraction and methylation (derivatization).

Table 2: Instrument Configuration and Analytical Conditions

GC system	Shimadzu GC-2030 with dual SPL, dual ECD-2030 Exceed and dual AOC-20 Plus autosampler
Column	Rtx-1701, 30m x 0.25mm x 0.25µm (line 1) Rxi5Sil-MS, 30m x 0.25mm x 0.25µm (line 2)
Injector Mode	Split at 1:1 ratio increase to 10 after 0.5 min
Injection Volume	1.5 µL
Carrier Gas	Helium
Flow mode	Constant pressure at initial linear velocity of 40cm/sec
Column Temp	35°C, 10min – 3°C/min – 65°C – 10°C/min – 85°C – 20°C/min – 205°C, 5min
Injection Port Temp	210°C
Detector Temp and Current	290°C, 2nA
Detector Gases	N2 15 mL/min, with Detector Constant Flow Mode

■ Results and Discussion

Using Shimadzu GC-2030 with dual inlet, detector and autosampler, nine methylated haloacetic acids and dalapon were analyzed simultaneously on an analytical column (Rtx-1701) and a confirmation column (Rxi5Sil-MS) according to EPA 552.3 method using helium as carrier gas. The list of analytes, identification number (for reference purposes) and their retention times on each column are shown in Table 3.

Results discussed in the subsequent sections demonstrate the system suitability of Shimadzu Nexis GC-2030 with ECD Exceed in accordance with the quality assurance and quality control criteria, including accuracy and precision, outlined in method EPA 552.3.

Table 3: List of compounds analyzed, Identification number and retention time in analytical and confirmation columns.

Compounds	Peak no.	Ret. Time (min)	
		Rtx-1701	Rxi5Sil-MS
MCAA	1	11.26	6.09
MBAA	2	16.03	10.02
Dalapon	3	16.53	12.62
DCAA	4	16.90	10.99
TCAA	5	20.24	16.56
1,2,3-trichloropropane (internal standard)	6	21.62	17.27
BCAA ^(*)	7	21.93	17.00
2-bromobutanoic acid (surrogate)	8	22.25	18.95
BDCAA ^(*)	9	23.79	22.07
DBAA	10	24.11	21.81
CDBAA ^(*)	11	25.40	24.43
TBAA ^(*)	12	26.71	25.86

^(*) Compounds included in HAA9 group

Method interferences: solvents

Prior to analyzing any sample, materials used in this analysis must be demonstrated to be free of interferences. Area counts of target analytes or other method interferences must be $\frac{1}{3}$ of the minimum reporting limit (MRL)². In this work, 1 ppb was the lowest concentration evaluated. The signal-to-noise ratio (S/N) was above 20 for all compounds at this concentration, exceeding the method requirement of $S/N \geq 5$.

The analytes for this project were purchased already derivatized; as a result, sample preparation consisted of dilution of standards with MTBE. A fresh aliquot of solvent was analyzed at the beginning of each analytical batch during the performance tests for the analysis of HAA5 and HAA9.

Figure 1 shows the overlaid chromatograms from the solvent blank and HAA5 standard (1 ppb) acquired with the analytical column (Rtx-1701; Figure 1a) and confirmation one (Rxi5Sil-MS; Figure 1b). Only two peaks within the range of where haloacetic acids elute were detected in the solvent blank on both columns (noted with an asterisk in the figure). These peaks do not coelute with target analytes or interfere with their quantification.

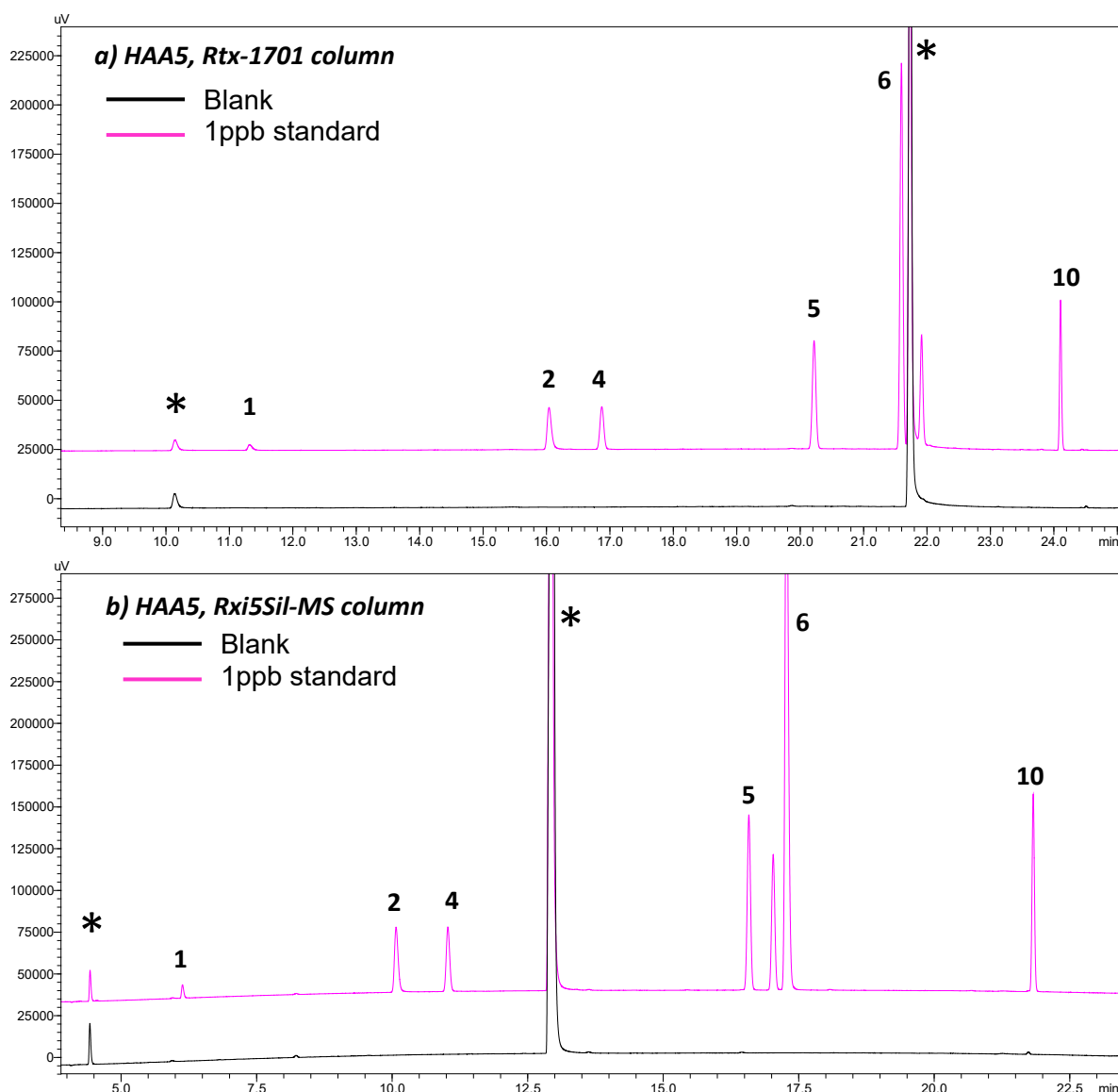


Figure 1: Chromatograms of MTBE blanks and 1ppb HAA Methyl Ester Mix #1 on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS).

The same results were obtained during analysis of HAA9. As shown in Figure 2, no analyte peaks were detected in the blanks for HAA9.

While there are two peaks present in the blanks (noted with an asterisk in the figure) within the range where HAA9 and dalapon elute, these do not interfere with any of the analyte peaks in either the analytical column (Rtx-1701; Figure 2a) or confirmation column (Rxi5Sil-MS; Figure 2b).

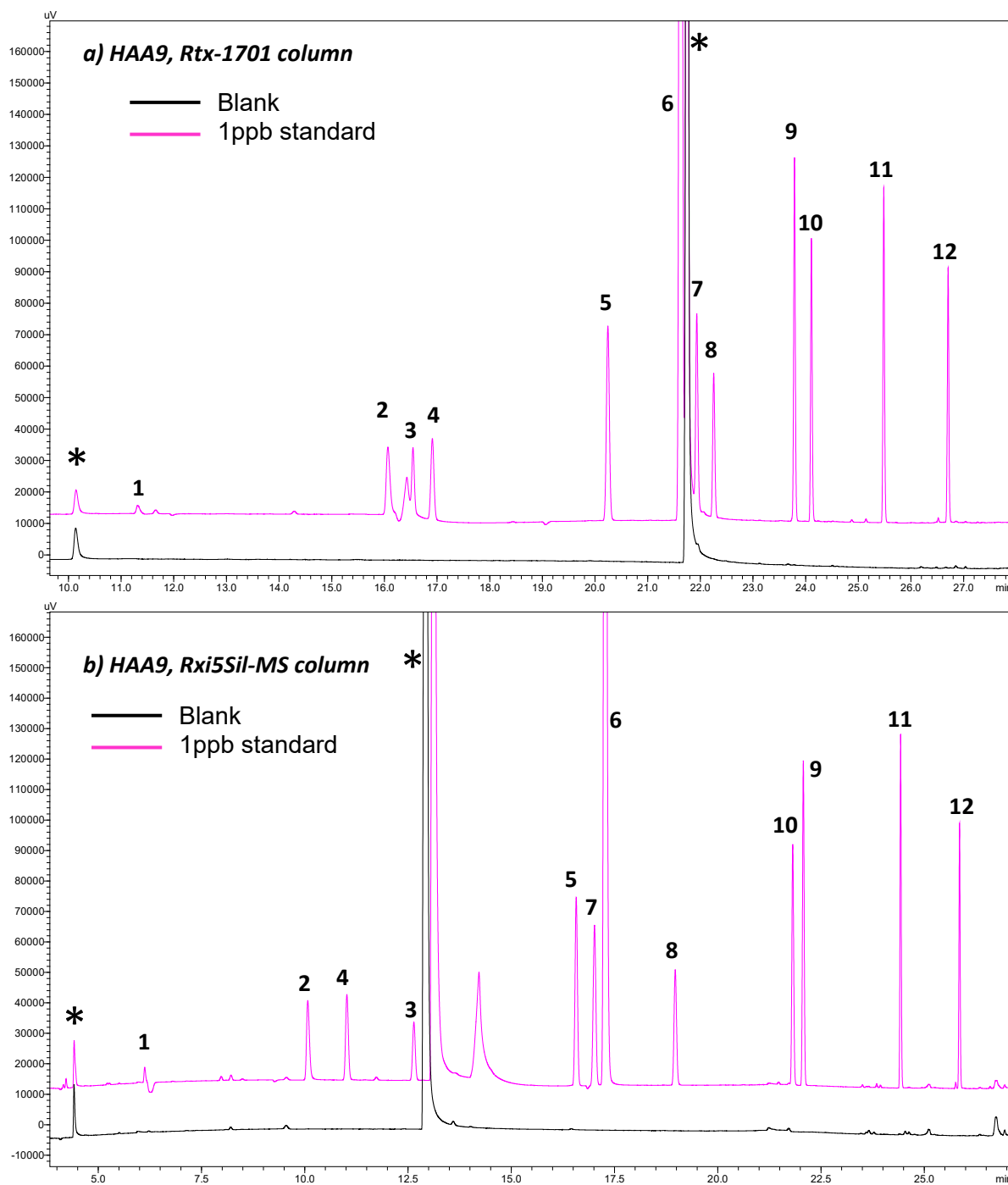


Figure 2: Chromatograms of MTBE blanks and 1ppb HAA Methyl Ester Mix #2 on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS). The results shown in Figures 1 and 2 confirmed the suitability of our system for demonstrating its performance for the analysis of HAA5 and HAA9.

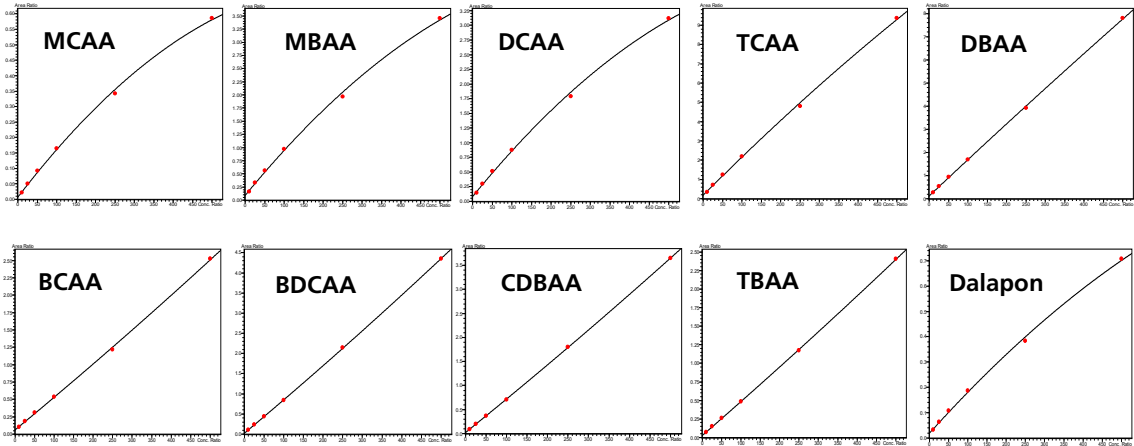
Calibration Curve

Method EPA 552.3 requires at least five calibration standards for preparing the initial calibration curves, with the lowest calibration standard at or below the MRL². In this study, a six-point calibration was used. The HAA methyl ester mix #1 and HAA methyl ester mix #2 were diluted to prepare the six calibration standards with concentrations ranging from 1 to 50 µg/L (in water sample).

Internal standard calibrations fitted quadratically with 1/A weighting without forcing through zero were built for all targets, in accordance with acceptable options included in method EPA 552.3.

The HAA5 and HAA9 calibration curves are shown in Figure 3 on the analytical (Figure 3a) and confirmation (Figure 3b) columns.

a) Rtx-1701



b) Rxi5Sil-MS

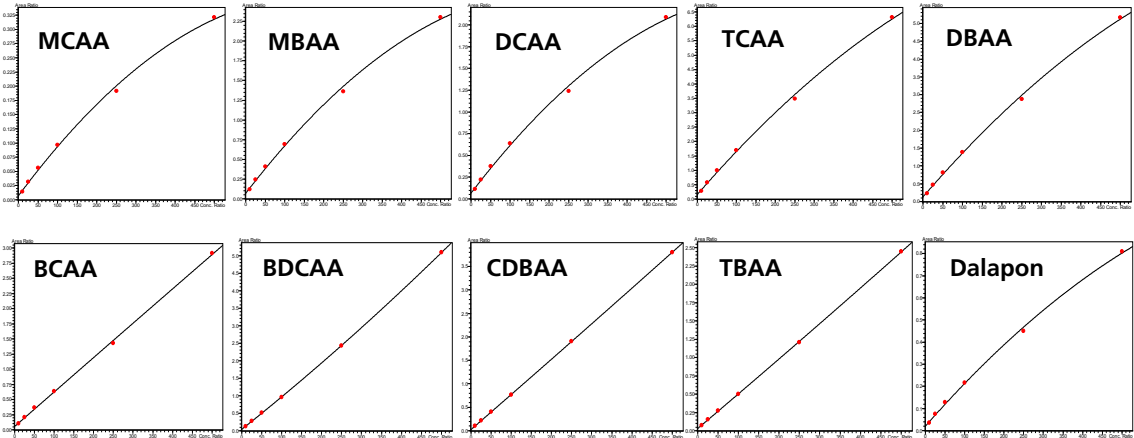


Figure 3: Six-point calibration curves for HAA5 on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS).

To proceed with the analysis of samples, accuracy of the calibration curve needs to be demonstrated. Per criteria outlined in method EPA 552.3, the analyte concentrations should be within 70-130% of the expected values, except for the lowest calibration level, for which results within 50-150% of expected values are accepted².

As shown in Table 4, all concentrations measured were within ± 22% of expected values. Hence, all results met and exceeded the accuracy ranges established by EPA, including the lowest calibration level (1 ppb).

Table 4: Calibration curve percent accuracy of measured concentrations.

Expected conc.	1 ppb		2.5 ppb		5 ppb		10 ppb		25 ppb		50 ppb	
	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2
MCAA	89.9	82.1	103.9	106.7	105.3	109.5	102.7	102.0	96.4	95.6	100.9	101.2
MBAA	82.2	80.0	107.1	107.5	107.2	109.9	103.3	101.8	95.6	95.8	101.1	101.1
DCAA	82.7	79.5	108.4	107.2	107.5	109.9	103.0	102.6	95.6	95.4	101.7	101.1
TCAA	83.8	86.0	106.9	105.6	106.7	107.4	101.8	100.7	96.8	97.4	100.7	100.5
DBAA	90.7	86.7	105.1	105.9	103.9	106.3	99.7	100.5	98.7	97.7	100.3	100.5
BCAA	81.4	81.7	106.8	107.0	106.9	108.5	101.8	101.7	97.0	96.5	100.6	100.8
BDCAA	99.1	95.5	102.0	103.2	99.6	101.7	98.7	99.3	100.7	99.6	99.9	100.1
CDBAA	98.2	98.7	102.1	101.9	100.0	100.1	98.7	98.9	100.5	100.4	99.9	99.9
TBAA	90.8	91.8	105.3	104.8	103.7	103.5	99.6	99.2	98.8%	99.1	100.3	100.2
Dalapon	78.2	79.3	109.0	107.9	108.1	110.1	103.3	102.0	95.3%	95.5	101.2	101.2

Additionally, although not required by EPA in method 552.3, coefficients of determination were calculated for all target analytes. As shown in the results in Table 5, fittings with $r^2 > 0.997$ were obtained for all analytes.

Table 5: Coefficient of determination (r^2) of the calibration curves.

Compounds	r^2	
	Rtx-1701	Rxi5Sil-MS
MCAA	0.998	0.997
MBAA	0.998	0.997
DCAA	0.998	0.997
TCAA	0.999	0.998
DBAA	0.999	0.998
BCAA	0.999	0.999
BDCAA	1.000	1.000
CDBAA	1.000	1.000
TBAA	1.000	1.000
Dalapon	0.998	0.998

Accuracy and precision

Accuracy and precision must be also demonstrated prior to analyzing samples by method EPA 552.3, especially in instances when a full initial calibration curve is not analyzed, based on the results from a mid-range level quality control sample ². For this purpose, a 10ppb standard (mid-range in calibration curve) containing the HAA5 was analyzed in replicates in three consecutive analytical batches (total n=17). The concentration of the analytes, summarized in Table 6, was within 4% of the expected value for all analytes, meeting and exceeding EPA's accuracy criteria (mean recovery within $\pm 20\%$). Also, as shown in Table 6, RSD for the HAA5 were less than 2%, greatly exceeding by an order of magnitude the EPA requirement for precision ($\leq 20\%$ RSD).

Table 6: Repeatability (%RSD, n=17) of 10 ppb (mid-range) standard over three analytical batches.

Compounds	Rtx-1701		Rxi5Sil-MS	
	Mean % recovery	%RSD	Mean % recovery	%RSD
MCAA	102.14	1.482	100.24	0.858
MBAA	103.26	1.711	101.66	0.988
DCAA	103.26	1.485	101.16	0.814
TCAA	103.36	1.274	100.66	0.882
DBAA	103.58	1.326	102.12	0.568

Data was further evaluated for accuracy and precision at the MRL (1ppb). As shown in Table 7, %RSD for all compounds at 1ppb were less than 11%, exceeding the EPA's precision requirement ($\leq 20\%$ RSD). For the lowest standard of the calibration curve, measured concentration must be within $\pm 50\%$ of the expected value; all HAA9 and dalapon exceeded this criteria and, furthermore, accuracy was within $\pm 20\%$ for the majority of the compounds.

Table 7: Repeatability (%RSD, n=3) of 1 ppb (lowest concentration) standard.

Compounds	Rtx-1701		Rxi5Sil-MS	
	Mean % recovery	%RSD	Mean % recovery	%RSD
MCAA	95.42	5.038	89.62	7.843
MBAA	87.89	5.582	83.37	3.453
DCAA	91.05	9.193	83.32	3.981
TCAA	101.72	1.474	123.28	2.726
DBAA	115.45	3.833	108.32	3.323
BCAA	110.00	6.671	82.86	4.984
BDCAA	124.29	2.612	137.62	1.670
CDBAA	121.32	2.818	107.15	2.760
TBAA	111.64	3.250	103.67	2.494
Dalapon	82.54	10.119	83.30	4.127

■ Additional Considerations for Ensuring Instrument Performance

To ensure the performance of the GC system and adherence to the quality assurance and quality control criteria outlined in method EPA 552.3, laboratories must carry out routine maintenance procedures. These include changing injection port septum and glass liners, trimming and replacing analytical and confirmation columns, and replacing gas filters. Improper maintenance operations normally lead to poor analytical results, potential damage of consumables and instrumentation, and, ultimately, increase the need for sample reanalysis and turn-around-time.

Oftentimes, leaks can develop after the routine tasks mentioned above, due to improper tightening of the ferrules and nuts. And leaks are one of the most common and detrimental problems in a GC system. In a GC-ECD system for HAA analysis, leaks could introduce oxygen into the system. Coupled with the high temperatures used in HAA analysis, the presence of oxygen could lead to oxidation of the column stationary phase and the ECD nickel foil, resulting in a need for replacing them.

Shimadzu Nexis GC-2030 is equipped with the innovative ClickTek technology for injection port top and column connections. The ClickTek adaptor allows users to secure inlet liners and commonly available fused silica capillary GC columns with a simple “twist and click”, minimizing the risk of damaging leaks. For additional confidence, the system has an automatic leak check function built into the GC firmware.

Gas filters are essential for the GC to perform at the optimal level. Regular replacement of gas filters for supply gases as well as filters on the split line of the split/splitless injection port. Shimadzu Nexis GC-2030 uses visible filters that can be easily replaced without any tools (Figure 4) at the end of their lives.

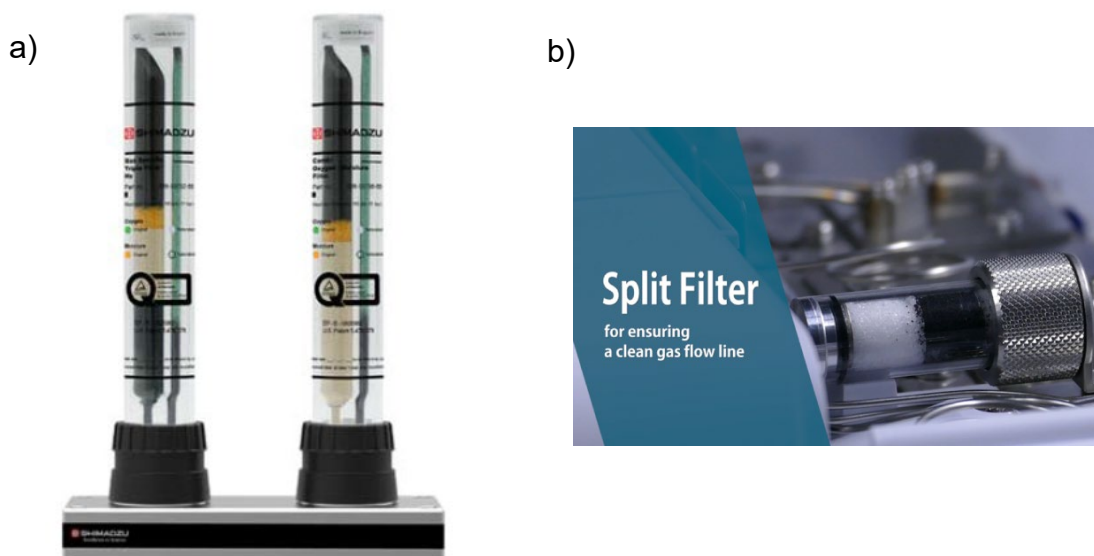


Figure 4: Gas filters for Nexis GC-2030 SPL ECD system. a) Super-clean gas filter set for supply gases (helium carrier gas and nitrogen makeup gas); b) split filter for Nexis GC-2030 SPL injection port.

■ Conclusion

Nexis GC-2030 with dual line split/splitless injectors and ECDs, equipped with ClickTek technology for ease of use, was employed to analyze HAA5, HAA9 and dalapon according to EPA method 552.3 and using helium as carrier gas. The dual line setup allows for the simultaneous quantitation of compounds on the analytical column and the confirmation column, increasing the throughput. The results obtained, in terms of accuracy and precision, met and exceeded EPA quality assurance I requirements, demonstrating the excellent performance and robustness of the system.

■ References

1. EPA the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) Fact Sheet for Assessment Monitoring – Haloacetic Acid (HAA) (2016)
2. EPA method 552.3, Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection, EPA 815-B-03-002 (2003)

■ Consumables

Part Number	Description	Unit	Instrument
221-76650-01	Septa, Green, Premium Low Bleed	Pk of 25	GC-2030
Restek 23322	Topaz Liner, Single Taper with Wool	Pk of 5	
221-81162-01	ClickTek Ferrule 0.4 mm	Pk of 6	
221-77155-41	ClickTek Column Connector	each	
221-34618-00	Syringe, 10 µL, fixed needle	each	AOC-20i/s
220-97331-31	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 100	
220-97331-47	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 1000	
220-97331-63	200 µL Glass Silanized Inserts for 1.5mL Vials	Pk of 100	
220-97331-23	Wash Vials, 4 mL Amber Glass with Caps & Septa	Pk of 100	

First Edition: February 2020



SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com

For Research Use Only. Not for use in diagnostic procedure.
This publication may contain references to products that are not available in your country. Please contact us to check the availability of these products in your country.

The content of this publication shall not be reproduced, altered or sold for any commercial purpose without the written approval of Shimadzu. Shimadzu disclaims any proprietary interest in trademarks and trade names used in this publication other than its own. See <http://www.shimadzu.com/about/trademarks/index.html> for details.

The information contained herein is provided to you "as is" without warranty of any kind including without limitation warranties as to its accuracy or completeness. Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to the use of this publication. This publication is based upon the information available to Shimadzu on or before the date of publication, and subject