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Application News

No. GC-2002

Gas Chromatography

Determination of Haloacetic Acids in Drinking Water According to EPA Method 552.3 using Hydrogen Carrier Gas

■ 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]. Whether the targets are HAA5 or HAA9, this analysis will continue to be performed regularly in environmental labs. Helium is specified as the carrier gas in EPA method 552, commonly used for HAA analysis in drinking water. Due to the increasing cost of helium, many labs are seeking alternative and affordable carrier gases to meet the monitoring requirements for HAAs. Here, we demonstrate the performance of EPA method 552.3 for the analysis of HAA9 using Shimadzu GC-2030 with dual line micro ECD setup. Hydrogen carrier gas is tested and shown to be a cost-effective alternative carrier gas for this method.

■ 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 (2018-2020)[1]. EPA method 552.3 is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon[1,2].

Table 1: List of HAAs included in EPA 552.3[2]

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

Traditionally these compounds were analyzed using helium (He) carrier gas, the cost of which has increased tremendously over the years. Hydrogen (H_2) has a lower molecular mass than He and its optimal linear velocity based on Van Deemter's plot is faster than that of He. This means no efficiency nor speed of analysis should be lost when using H_2 carrier gas instead of He. In addition, current price of H_2 gas is approximately three to six times lower than the price of He, due to the limited availability of the later. This makes H_2 an ideal alternative carrier gas for HAA analysis. In this application, we explored using H_2 carrier gas to determine HAA concentrations according to EPA method 552.3.

■ Materials and Methods

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

A Shimadzu GC-2030 with dual line split/splitless injector, dual ECD-exceed detector and dual autosampler was used for analysis of haloacetic acids and dalapon according to EPA method 552.3. Haloacetic acid methyl ester mix with internal standard was run on the GC system. The concentration indicated in Results and Discussion represent the original concentration of each compound in water before extraction and methylation (derivatization). The extraction process results in a sample concentration 10 times that of the original concentration in water.

Analysis conditions are outlined in Table 2 below. LabSolutions software was used for data acquisition and processing.

Nexis GC-2030

■ Results and Discussion

We had previously analyzed methylated HAA9, dalapon and surrogate simultaneously on an analytical column (Rtx-1701) and a confirmation column (Rxi5Sil-MS) according to EPA 552.3 method using Shimadzu GC-2030 with dual inlet, detector and autosampler with He carrier gas [3]. With the dual line setup, the EPA required quantification and confirmation of HAAs and dalapon can be completed in one GC run. In this application, we compared the chromatogram of HAAs and dalapon using H_2 to that using He, as well as assessed the performance of the same instrument setup using H_2 carrier gas per EPA 552.3 criteria.

Comparison of H_2 carrier gas to He carrier gas.
The chromatograms obtained with H_2 carrier gas were compared to those obtained with He carrier gas. The same instrument settings including the flow parameters (constant pressure at initial linear velocity of 40cm/sec) were used. The chromatograms of HAA using H_2 carrier gas were nearly identical to those using He carrier gas. The retention times of each compound using H_2 or He carrier gas were shown in Table 3 below. The differences are minimal.

Table 2: Instrument Configuration and Analysis Conditions

GC system	Shimadzu Nexis 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 0.5min
Injection Volume	1.5 µL
Carrier Gas	Hydrogen
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	N_2 15mL/min, with Detector Constant Flow Mode

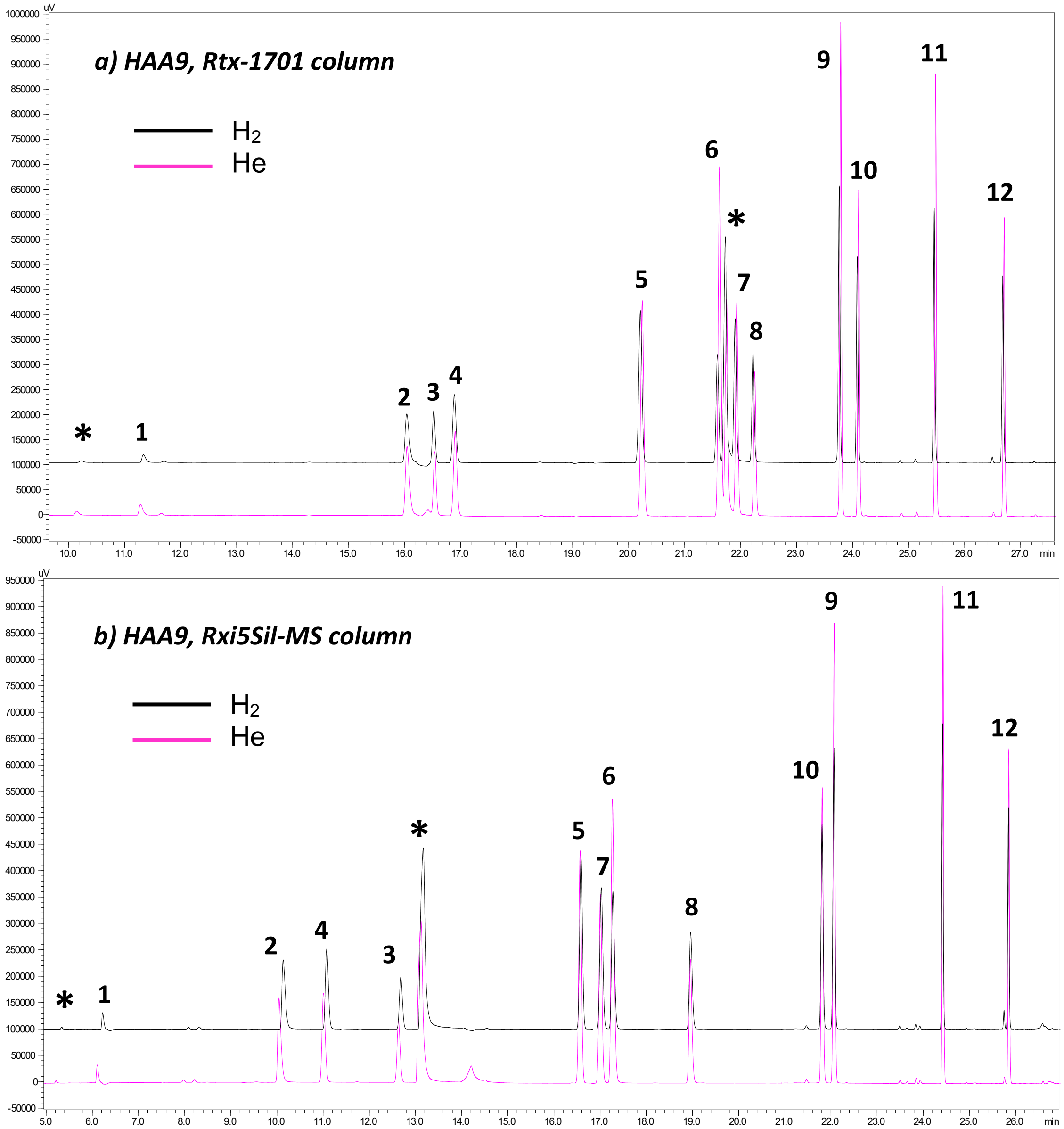


Figure 1: Chromatograms of 10 ppb HAA Methyl Ester Mix analyzed with indicated carrier gas on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS). Peaks indicated with an asterisk do not correspond to any of target peaks.

Table 3: List of compounds analyzed and the retention times with different carrier gases.

Compounds	Peak no.	Ret. Time (min) on Rtx-1701		Ret. Time (min) on Rxi5Sil-MS	
		H_2 Carrier	He Carrier	H_2 Carrier	He Carrier
MCAA	**1**	11.32	11.26	6.12	6.09
MBAA	**2**	16.06	16.03	10.07	10.02
Dalapon	**3**	16.54	16.53	12.64	12.62
DCAA	**4**	16.91	16.90	11.01	10.99
TCAA	**5**	20.24	20.24	16.57	16.56
1,2,3-Trichloropropane (internal standard)	**6**	21.63	21.62	17.26	17.27
BCAA (*)	**7**	21.93	21.93	17.01	17.00
2-Bromobutanoic acid (surrogate)	**8**	22.25	22.25	18.97	18.95
BDCAA (*)	**9**	23.79	23.79	22.07	22.07
DBAA	**10**	24.11	24.11	21.81	21.81
CDBAA (*)	**11**	25.48	25.40	24.43	24.43
TBAA (*)	**12**	26.71	26.71	25.85	25.86

(*) Compounds included in HAA9 group

Method interferences: solvents

Using H_2 carrier gas, MTBE blanks were analyzed at the beginning of each sample run. As shown in Figure 2, the results are within the acceptable criteria for the presence of targets in the blanks listed in EPA method 552.3, which is below 1/3 of the minimal reporting level (1 ppb).

There are two peaks (marked with asterisks) present in the blanks that do not coelute with any of the analyte peaks.

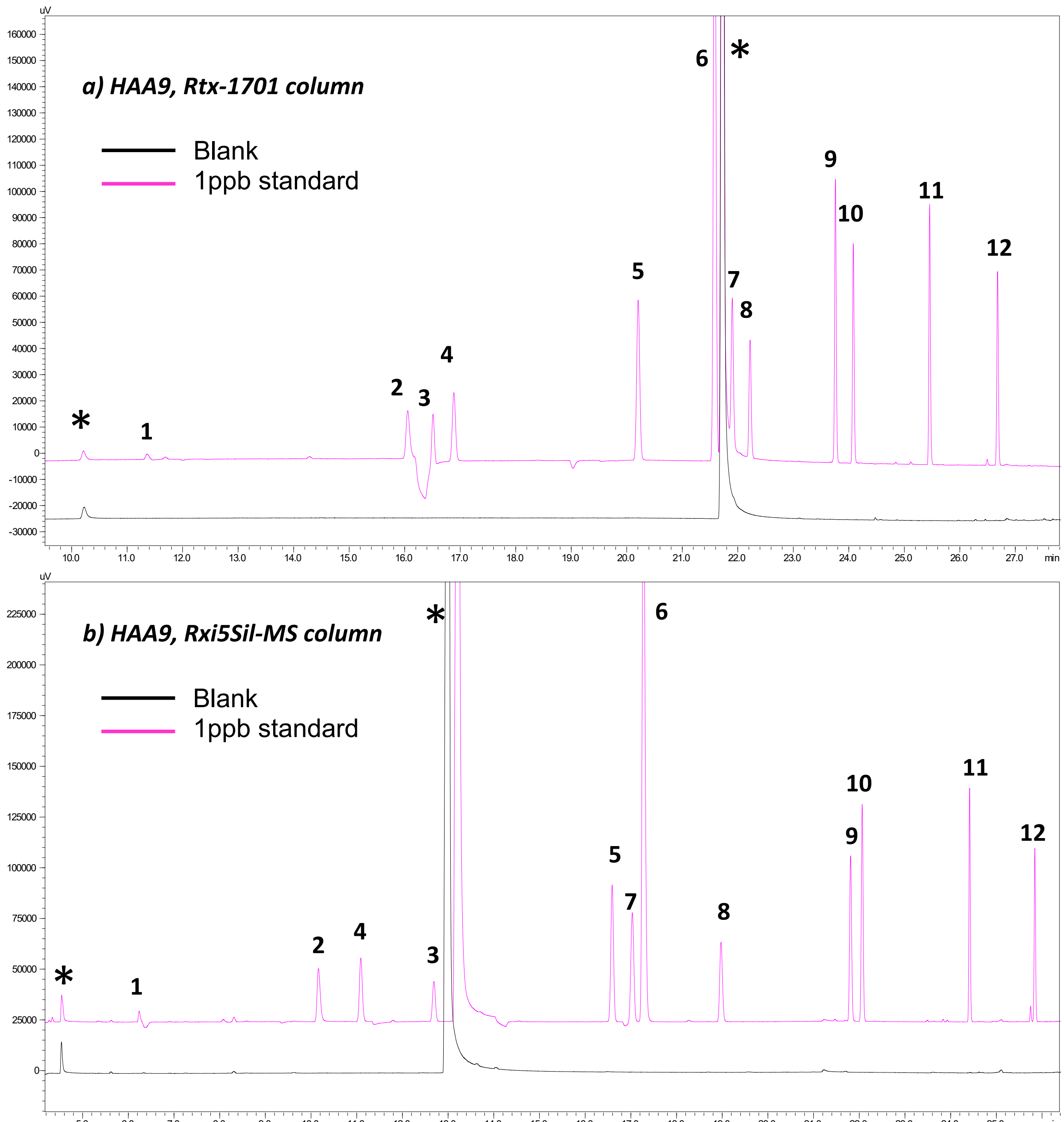


Figure 2: Chromatograms of MTBE blanks and 1 ppb HAA Methyl Ester Mix on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS) using H_2 carrier gas. Peaks indicated with an asterisk do not correspond to any of target peaks.

Calibration Curves with H_2 Carrier Gas:
The HAA methyl ester mix was diluted to prepare a six-point calibration curve with concentrations from 1 to 50 ppb in water. Internal standard calibrations fitted quadratically with 1/A weighting without forcing through zero were built for all targets.

The calibration curves and the coefficients of determination (r^2 Values) are shown in Figure 3 and Table 4. All r^2 values were higher than 0.995.

Table 4: Coefficient of determination (r^2) of the calibration curves.

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

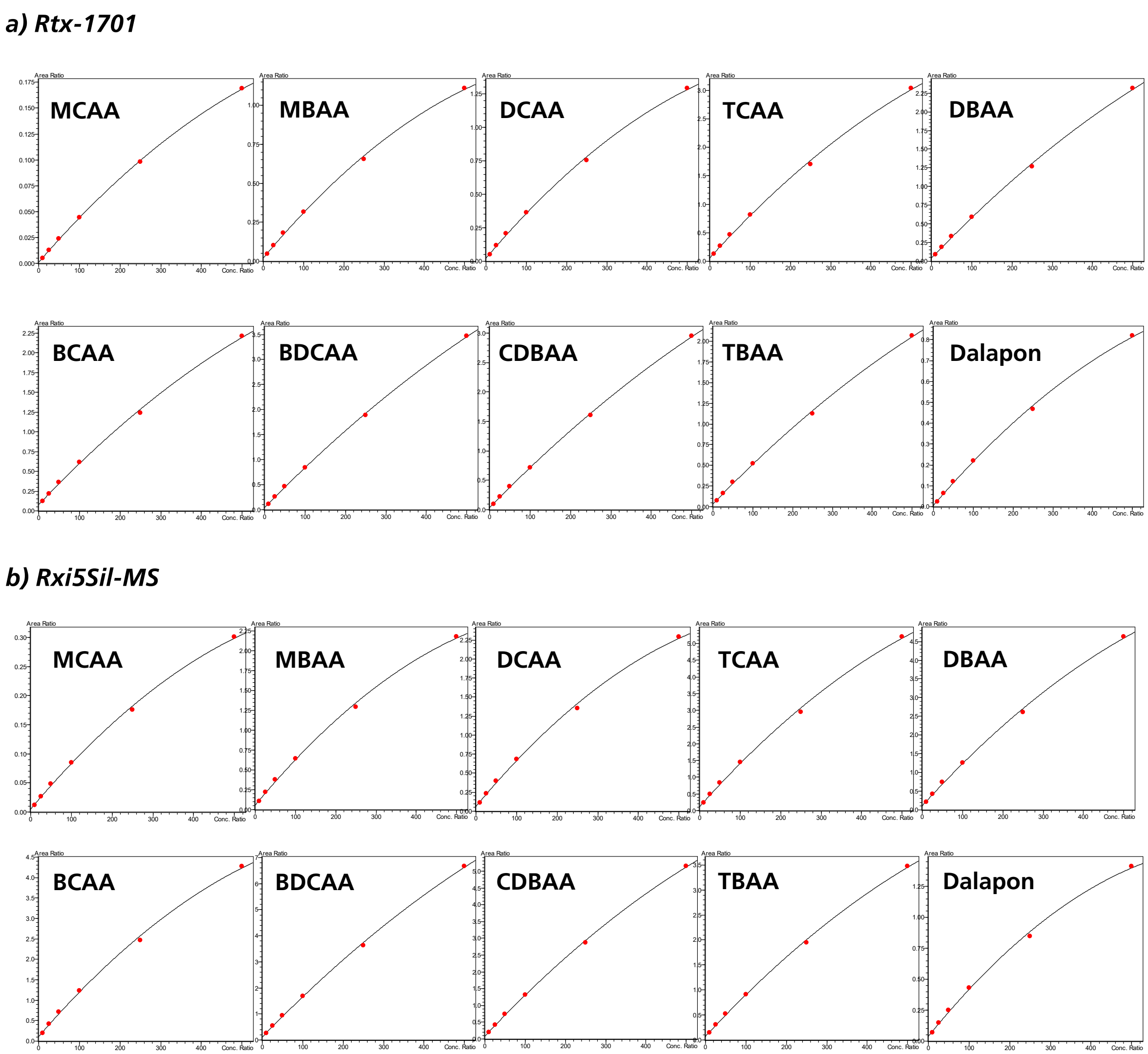


Figure 3: Six-point calibration curves for HAA5 on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS) using H_2 carrier gas.

The method requires demonstration of calibration accuracy. Specifically, the analyte concentrations should be within ±30% of the expected values, except for lowest calibration level, where ±50% is acceptable. In other words, the measured concentrations should be within 70 - 130% of expected values (or with 50 - 150% for the lowest calibration level). In Table 5, the percentage of measured concentrations over expected values (percent recovery) are summarized. Based on the results shown, it can be concluded that all results were well within EPA's acceptable range and difference were < ±25% for the lowest calibration level and < ±10% for all other levels.

Repeatability

The 1 ppb standard was injected three times and the percent RSD was calculated. As shown in Table 6 below, all are under 2% RSD, greatly exceeding the EPA requirement of less than 20% RSD. The percent recovery required for MDL is ±50% of the expected value. As shown in Table 6, the mean % recovery for all compounds ranged from 76.84 to 93.80, within 25% of the expected value of 1 ppb.

Table 5: Calibration accuracy results (based on percent recoveries) at each calibration level.

Expected conc.	1ppb		2.5ppb		5ppb		10ppb		25ppb		50ppb	
	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2	Line1	Line2
MCAA	94.5	84.1	103.1	107.5	102.3	107.7	101.2	102.5	98.1	95.5	100.5	101.4
MBAA	84.8	80.1	107.3	107.8	106.6	109.1	102.2	103.1	96.0	94.9	101.3	101.7
DCAA	83.8	78.7	107.6	109.0	107.6	108.9	102.4	103.4	95.6	94.7	101.4	101.7
TCAA	82.1	79.6	107.8	108.8	108.1	108.8	102.6	102.9	95.6	95.1	101.2	101.4
DBAA	84.0	79.4	107.6	108.9	106.9	109.0	101.7	102.6	96.4	95.3	100.9	101.3
BCAA	80.3	78.5	105.7	109.0	107.8	109.2	103.3	103.3	95.8	94.8	101.1	101.6
BDCAA	88.9	84.9	105.9	107.7	105.1	106.3	100.8	101.2	97.5	96.8	100.6	100.8
CDBAA	89.2	87.0	105.4	107.0	105.3	104.9	100.7	101.2	97.6	97.2	100.6	100.7
TBAA	84.8	83.5	107.0	108.0	107.2	106.7	101.7	101.5	96.4	96.5	100.9	100.9
Dalapon	86.3	78.2	108.3	109.4	107.2	109.1	102.0	103.5	95.7	94.5	101.3	101.9

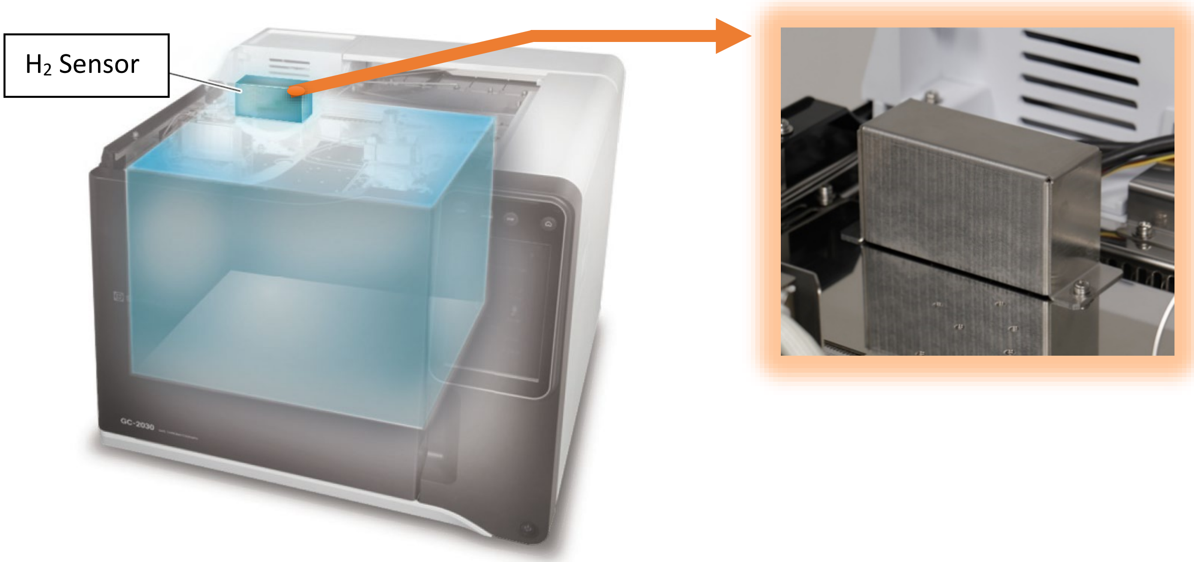
Table 6: Repeatability (%RSD, n=3) and mean % recovery of 1 ppb (MDL concentration) standard.

Compounds	Rtx-1701		Rxi5Sil-MS	
	Mean % recovery	%RSD	Mean % recovery	%RSD
MCAA	93.80	0.67	84.62	1.19
MBAA	83.54	1.34	78.69	1.58
DCAA	82.63	1.24	77.14	1.80
TCAA	81.13	1.15	78.82	0.95
DBAA	83.23	0.86	78.40	1.42
BCAA	80.20	1.72	77.17	1.65
BDCAA	88.32	0.59	84.15	0.81
CDBAA	88.51	0.64	86.32	0.81
TBAA	84.14	0.83	82.82	0.77
Dalapon	86.92	0.70	76.84	1.62

Cost savings by switching to hydrogen carrier gas

Based on the current market prices for He and H_2, cost of analysis, when switching from He to H_2 as carrier gas, will decrease approximately between 3 and 6 times, depending on the gas grade used. One concern about switching carrier gas is the safety of using H_2 gas, as it is flammable. To address this concern, the Nexis GC-2030 offers an integrated H_2 sensor to detect the presence of H_2 in the GC oven.

If H_2 concentration inside oven is above 0.4%, an error message will appear, and the GC will automatically vent and shut down its heat control. At 2% the system will completely shut off to allow H_2 to dissipate before reaching the explosion threshold of 4%. In addition, GC-2030 features an automatic carrier gas leak check function that allows users to run a H_2 leak test at their desired frequency.



■ Conclusion

Hydrogen carrier gas was used successfully to analyze HAA9 compounds according to EPA method 552.3 on Nexis GC-2030 with dual line split/splitless injectors and ECDs. The results obtained met and exceeded EPA's quality assurance requirements for HAA9 and dalapon, proving that H_2 is a suitable alternative carrier gas to He.

Based on the current market prices for both gases, cost of analysis, when switching from He to H_2 carrier gas, will decrease approximately 6 times when using Research Grade (99.9999%) gas or 3 times when using Ultra High Purity (99.999%).

Additionally, laboratories will avoid potential restrictions in He purchasing that are being more frequently implemented by gas suppliers. Moreover, H_2 can be easily generated by gas generators, eliminating of the need for gas tanks altogether. Safety concerns regarding the use of H_2 can easily be minimized with the safety features of Nexis GC-2030.

■ References

1. 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)
2. EPA the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) Fact Sheet for Assessment Monitoring – Haloacetic Acid (HAA) (2016)
3. Determination of Haloacetic Acids (HAA5 and HAA9) in Drinking Water According to EPA Method 552.3, Shimadzu Application News GC-009 (2020)

■ 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 0.4mm	Pk of 6	
221-77155-41	ClickTek Column Connector	each	
221-34618-00	Syringe, 10µL, fixed needle	each	AOC-20i/s
220-97331-31	Sample Vials, 1.5mL Amber Glass with Caps & Septa	Pk of 100	
220-97331-47	Sample Vials, 1.5mL Amber Glass with Caps & Septa	Pk of 1000	
220-97331-63	200µL Glass Silanized Inserts for 1.5mL Vials	Pk of 100	
220-97331-23	Wash Vials, 4mL Amber Glass with Caps & Septa	Pk of 100	

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