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Decreasing the Cost and Increasing the Efficiency of Analysis of Haloacetic Acids Using Hydrogen Carrier Gas and Alternative Columns

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Introduction

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently five HAAs (MCAA, MBAA, DCAA, TCAA, DBAA) are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR). 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 (Table 1) is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon[1,2].

Due to the increasing cost of helium (He), many labs are seeking alternative and affordable carrier gases to meet the monitoring requirements for HAAs. Hydrogen (H_2) carrier gas is tested here as carrier gas and an affordable alternative to helium for this method. We also tested Rtx-CLPesticides and Rtx-CLPesiticides2 columns (Rtx-CLP column set) as alternatives to the traditional 1701 and 5 phase columns. Not only does using the Rtx-CLP column set shortens the GC run time and increases efficiency, it also allows flexibility of the GC system to be used for multiple environmental analyses.

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

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		

Experimental

A Shimadzu Nexis 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 concentrations indicated in here 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.

Table 2: Instrument Configuration and Analysis Conditions

GC system	Shimadzu GC-2030 with dual SPL, dual ECD-2030 exceed and dual AOC-20 Plus autosampler
Carrier Gas	He or H_2
Column set 1	Rtx-1701, 30m x 0.25mm x 0.25µm (analytical) Rxi5Sil-MS, 30m x 0.25mm x 0.25µm (confirmation)
Column set 2	Rtx-CLPesticides, 30m x 0.32mm x 0.32µm (analytical) Rtx-CLPesticides2, 30m x 0.32mm x 0.25µm (confirmation)
Column Temp (set 1)	35°C, 10min – 3°C/min – 65°C – 10°C/min – 85°C – 20°C/min – 205°C, 5min
Column Temp (set 2)	35°C, 4min – 10°C/min – 250°C, 1min
Flow mode (set 1)	Constant pressure at initial linear velocity of 40cm/sec
Flow mode (set 2)	Constant initial linear velocity of 25cm/sec

Comparison of different carrier gas and column sets

The chromatograms obtained with H_2 carrier gas were compared to those obtained with He carrier gas. GC parameters were kept the same for this comparison. The chromatograms of HAAs using H_2 carrier gas were nearly identical to those using He carrier gas (Figure 1). The retention times of each compound using H_2 or He carrier gas are shown in Table 3 (right). The differences are minimal.

To increase the efficiency of the analysis, an alternative column set (Rtx-CLP and Rtx-CLP2) was tested using H_2 carrier gas. Compared to using the traditional 1701 and 5 phase columns, GC run time was shorten by over 10 min (Figure 2). The retention times on different columns are listed in Table 4 below.

Table 3: List of compounds analyzed and the retention times with different carrier gases on Column set 1 (Rtx-1701 and Rxi5Sil-MS).

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

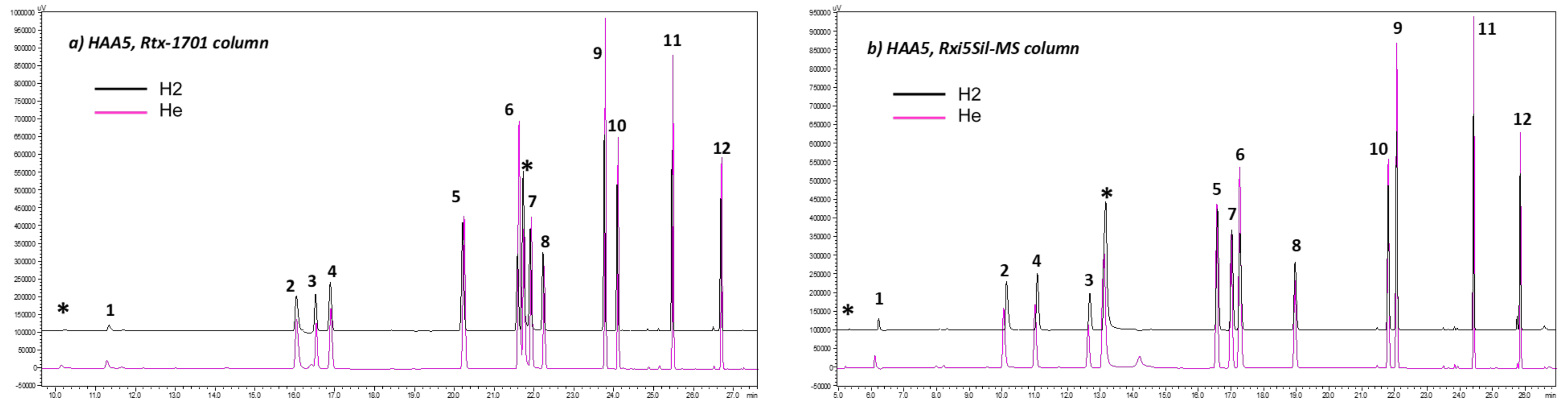

Figure 1: Chromatograms of 10 ppb HAA Methyl Ester Mix analyzed with indicated carrier gas on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS). Peaks indicated with an asterisk do not correspond to any of target peaks.

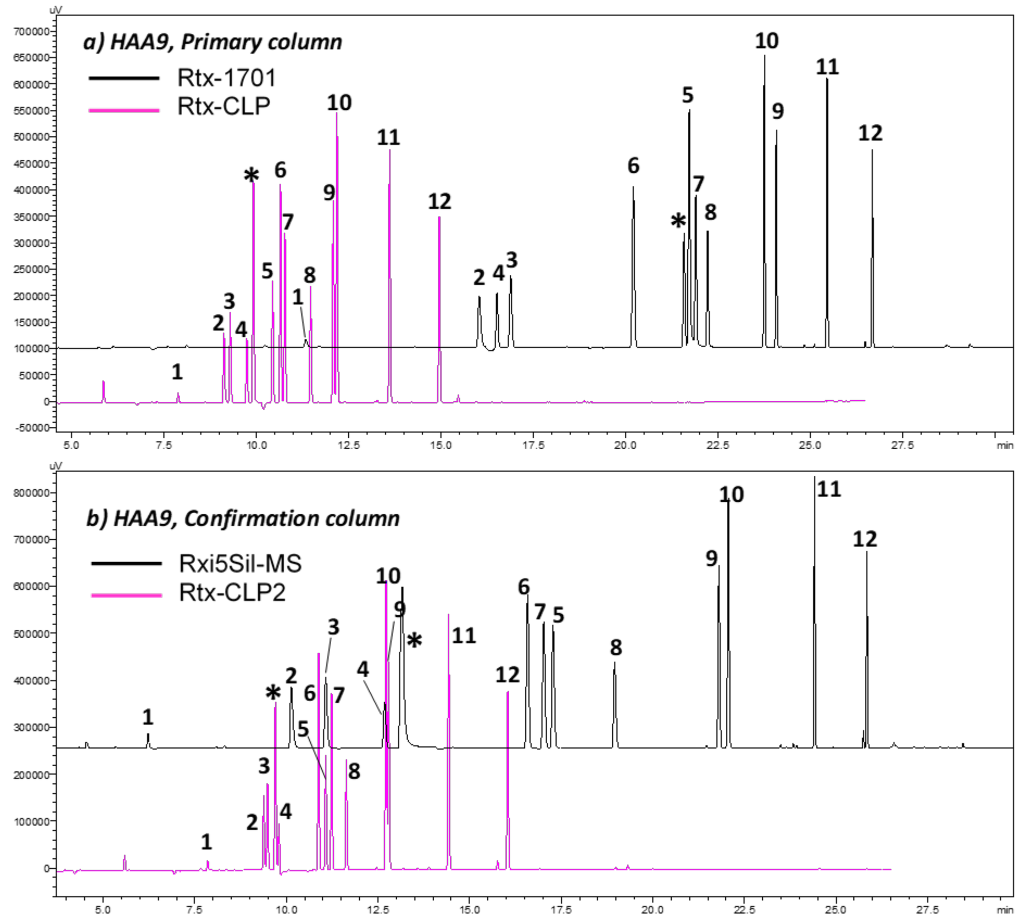

Table 4: List of compounds analyzed and the retention times on different columns.

Compounds	Peak no.	Ret. Time (min) on Primary Column		Ret. Time (min) on Confirmation Column	
		Rtx-1701	Rtx-CLP	Rxi5Sil-MS	Rtx-CLP2
MCAA	1	11.34	7.87	6.22	7.86
MBAA	2	16.04	9.12	10.14	9.38
DCAA	3	16.89	9.29	11.08	9.49
Dalapon	4	16.52	9.74	12.68	9.80
1,2,3-Trichloropropane (internal standard)	5	21.73	10.43	17.28	11.08
TCAA	6	20.21	10.66	16.59	10.88
BCAA (*)	7	21.90	10.77	17.03	11.24
2-Bromobutanoic acid (surrogate)	8	22.22	11.47	18.96	11.64
DBAA	9	24.08	12.09	21.81	12.79
BDCAA (*)	10	23.76	12.19	22.07	12.72
CDBAA (*)	11	25.46	13.62	24.42	14.43
TBAA (*)	12	26.68	14.96	25.84	16.04

(*) Compounds included in HAA9 group

Figure 2: Chromatograms of 10 ppb HAA Methyl Ester Mix analyzed on indicated a) analytical column and b) confirmation column. Peaks indicated with an asterisk do not correspond to any of target peaks.

EPA 552.3- Results using H_2 as carrier gas and Rtx-CLP columns

1. Blanks:

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 the method, which is below 1/3 of the minimal reporting level (1 ppb). There are two peaks (marked with asterisks) from unknown compounds present in the blanks that do not coelute with any of the analyte peaks.

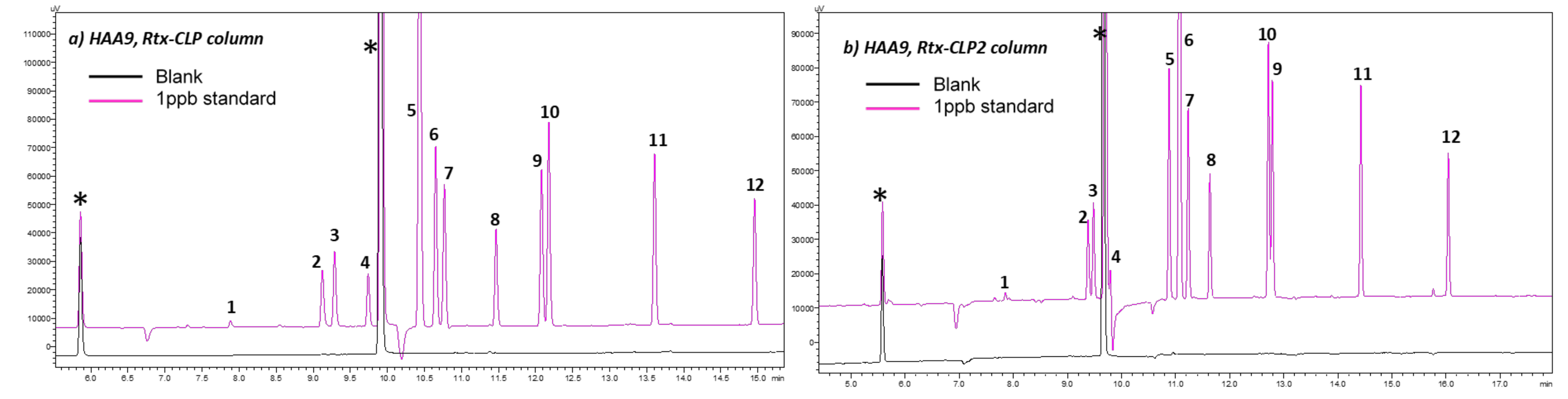

Figure 3: Chromatograms of MTBE blanks and 1 ppb HAA Methyl Ester Mix on a) analytical column (Rtx-CLP) and b) confirmation column (Rtx-CLP2) using H_2 carrier gas. Peaks indicated with an asterisk do not correspond to any of target peaks.

2. Calibration curves:

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 equal to or higher than 0.998.

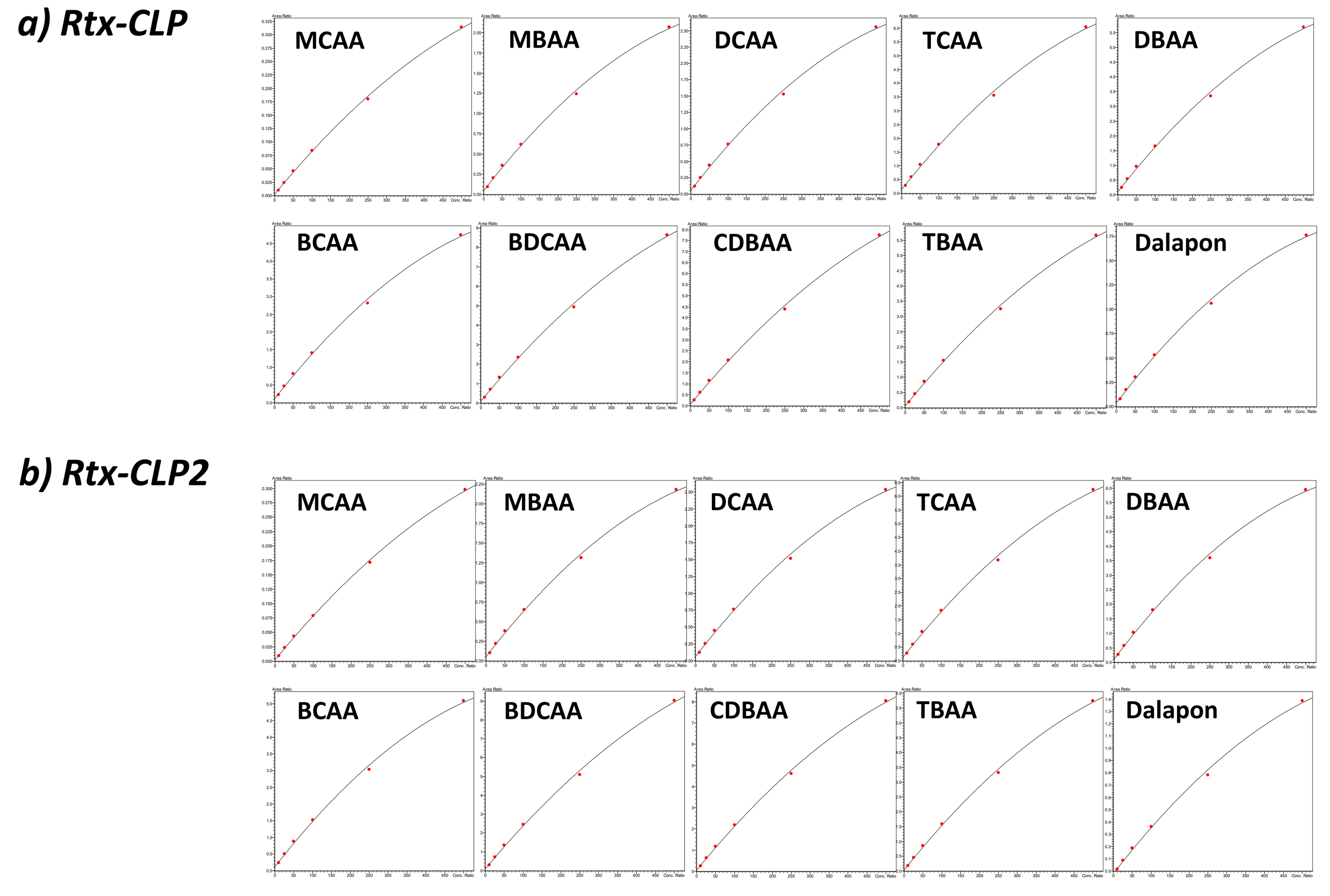

Figure 4. Six-point calibration curves for HAA9 and dalapon on a) analytical column (RtxCLP) and b) confirmation column (Rtx-CLP2) using H2 carrier gas.

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. The reported concentration of each level was checked, and as shown in Table 5, all results were within EPA's acceptable range (<±21% for the lowest calibration level and <±10% for all other levels).

Table 5. Calibration curve percent accuracy of measured concentrations.

Expected conc.	1ppb		2.5ppb		5ppb		10ppb		25ppb		50ppb	
	Rtx-CLP	Rtx-CLP2	Rtx-CLP	Rtx-CLP2	Rtx-CLP	Rtx-CLP2	Rtx-CLP	Rtx-CLP2	Rtx-CLP	Rtx-CLP2	Rtx-CLP	Rtx-CLP2
MCAA	89.6	89.7	104.9	105.4	106.3	105.7	101.7	101.4	96.5	96.8	101.0	100.9
MBAA	81.9	80.8	107.7	108.3	108.7	109.0	102.8	102.4	95.1	95.2	101.7	101.7
DCAA	81.5	79.5	107.3	108.4	109.0	109.5	103.1	103.1	94.8	94.7	101.8	101.8
TCAA	79.7	80.9	108.1	107.7	109.5	109.1	103.3	103.6	94.6	94.5	101.7	101.8
DBAA	82.4	83.6	107.4	106.6	109.1	108.0	103.1	103.5	94.8	94.8	101.7	101.9
BCAA	81.1	81.2	107.5	107.7	108.8	108.8	103.2	103.4	94.8	94.7	101.7	101.8
BDCAA	86.1	85.7	106.1	106.2	108.0	108.0	102.6	103.3	95.5	95.1	101.3	101.4
CDBAA	87.6	89.2	105.6	105.1	107.2	105.9	102.5	103.0	95.7	95.8	101.2	101.2
TBAA	86.4	89.4	105.8	105.5	108.3	105.3	102.8	103.6	95.3	95.5	101.4	101.4
Dalapon	82.1	92.6	107.5	111.7	108.7	107.6	103.0	102.4	94.9	94.2	101.8	102.0

Multiple Analyses using the Same System

The same GC dual line system with Rtx-CLP column set can be used for additional analyses such as organochlorine pesticides and herbicides. To demonstrate this capability, we analyzed organochlorine pesticides on Rtx-CLP column.

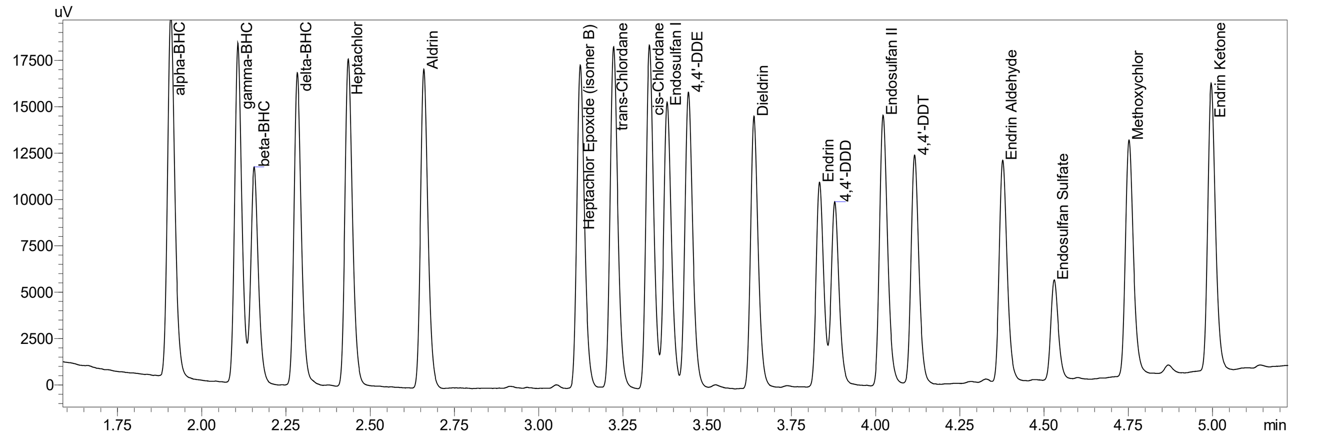

Figure 5. Chromatogram of 4 ppb organochlorine pesticides standard in hexane analyzed on Rtx-CLP column using He carrier gas.

Conclusion

Hydrogen carrier gas and Rtx-CLP column set were used successfully to assay 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 requirements for HAA9 and dalapon, proving that H_2 carrier gas and the CLP column set are suitable alternatives to the traditional EPA method set up. Not only was the GC system with the CLP column set suitable for determination of HAAs, it can also be used for additional EPA methods such as the analysis of organochlorine pesticides in environmental samples. In addition to replacing expensive He carrier gas with H_2 and faster analysis, the capability of using one system for multiple environmental analyses further decreases the operational cost.

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).