

Can we keep the cost of analysis of haloacetic acids (HAAs) down by using an alternative to Helium?

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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 have 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 (Table 1) is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon^{1,2}.

Traditionally these compounds were analyzed using helium (He) carrier gas, the cost of which has increased tremendously over the years. In this application, we explored using alternative hydrogen (H₂) carrier gas to determine HAA concentrations according to EPA method 552.3.

Table 1: List of HAAs included in EPA 552.3²

Compound	Acronyms	HAA Group	
Monochloroacetic acid	MCAA	HAA5	HAA9
Monobromoacetic acid	MBAA		
Dichloroacetic acid	DCAA		
Trichloroacetic acid	TCAA		
Dibromoacetic acid	DBAA		
Bromochloroacetic acid	BCAA	HAA9	
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
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 or 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	N ₂ 15mL/min, with Detector Constant Flow Mode

Comparison of hydrogen to helium as carrier gas

The chromatograms obtained with H₂ carrier gas were compared to those obtained with He carrier gas. For switching from hydrogen (H₂) carrier gas to helium (He) carrier gas, we kept the same instrument settings including the flow parameters (constant pressure at initial linear velocity of 40cm/sec). The chromatograms of HAAs using H₂ carrier gas were nearly identical to those using He carrier gas (Figure 1). The retention times of each compound using H₂ or He carrier gas were shown in Table 3. The differences are minimal.

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	
		H2 Carrier	He Carrier	H2 Carrier	He Carrier
		MCAA	1	11.32	11.26
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

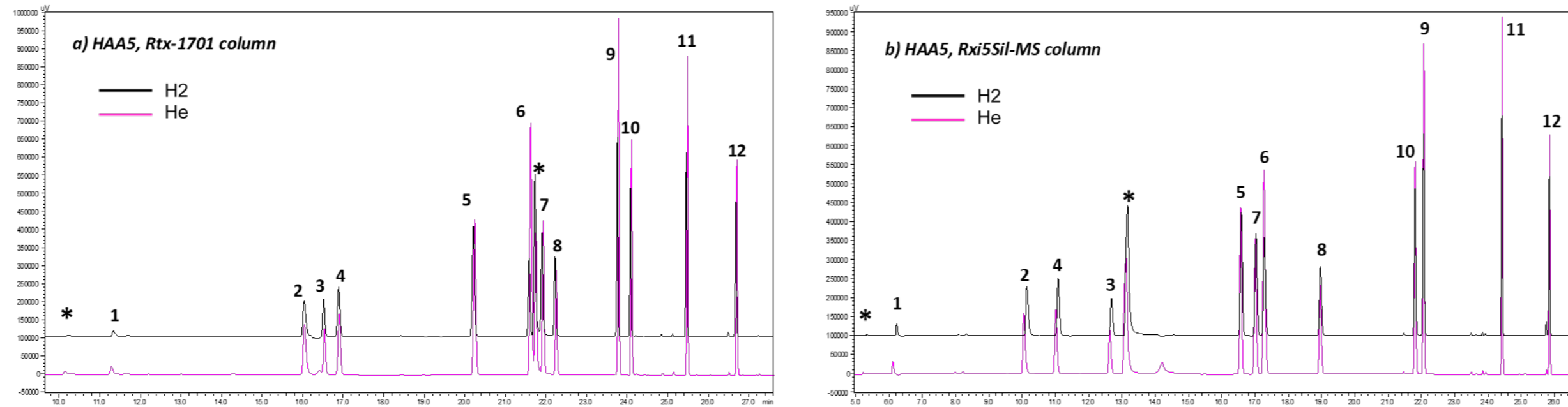


Figure 1: Chromatograms of 10 ppb HAA Methyl Ester Mix analyzed with indicated carrier gas on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS). Peaks indicated with an asterisk do not correspond to any of target peaks.

EPA 552.3- Results using H₂ as carrier gas

1. Blanks:

Using H₂ 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 (1ppb). There are two peaks (marked with asterisks) from unknown compounds present in the blanks that do not coelute with any of the analyte peaks.

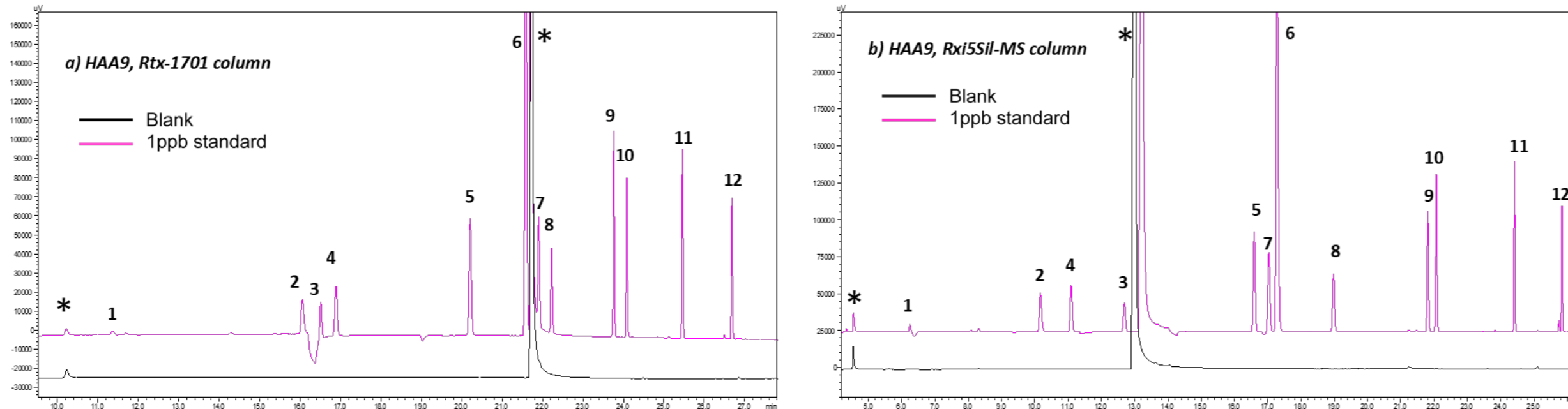
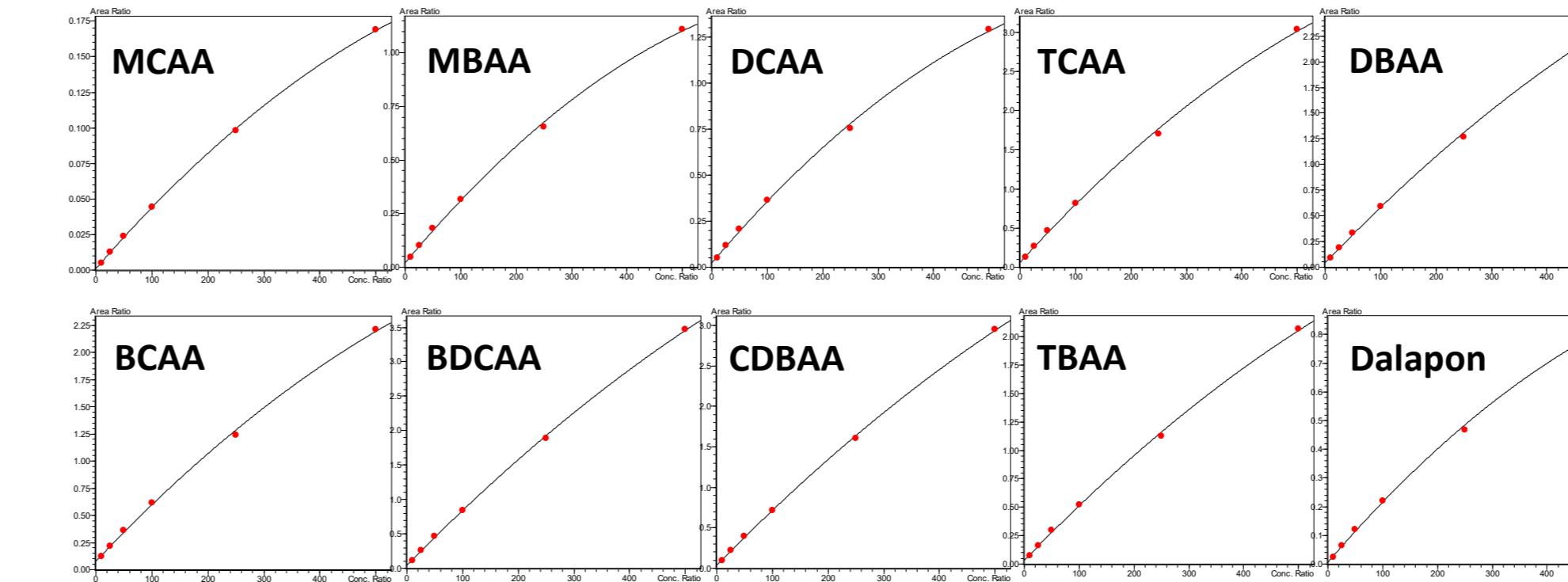


Figure 2: Chromatograms of MTBE blanks and 1 ppb HAA Methyl Ester Mix on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS) using H₂ carrier gas. Peaks indicated with an asterisk do not correspond to any of target peaks.

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 higher than 0.995.

a) Rtx-1701



b) Rxi5Sil-MS

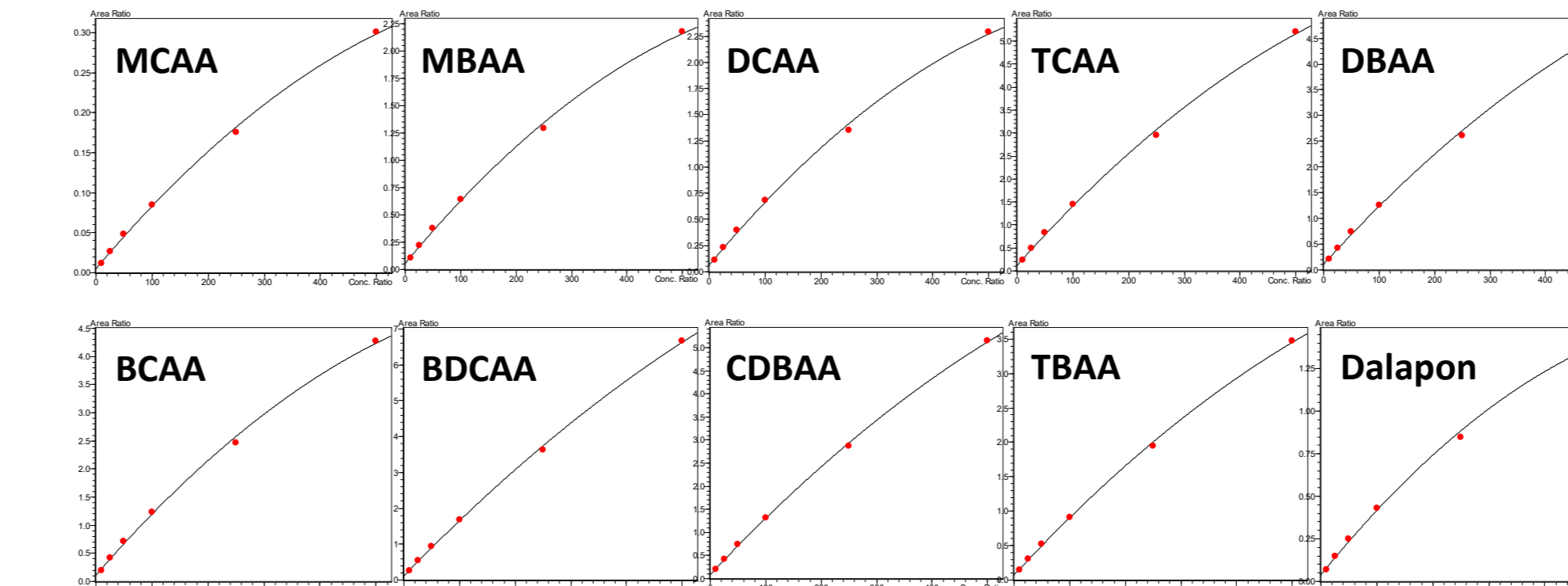


Figure 3: Six-point calibration curves for HAA5 on a) analytical column (Rtx-1701) and b) confirmation column (Rxi5Sil-MS) using H₂ carrier gas.

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

Compounds	<i>r</i> 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

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 (±30% of expected values).

Table 5: Calibration curve percent accuracy of measured concentrations.

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	107.7	101.5	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

3. Repeatability:

The 1 ppb standard was injected three times and the percent RSD was calculated. As shown in Table 6, all values 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 6: Repeatability results.

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

Conclusion

Hydrogen carrier gas was 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 H₂ is a suitable alternative carrier gas to helium. Based on current market prices for both gases, cost of analysis, when switching from helium to hydrogen as carrier gas will decrease approximately by 6.15 times when using Research Grade (99.9999%) gas or 2.69 times when using Ultra High Purity (99.999%). Additionally, laboratories will avoid potential restrictions in helium purchasing that are being more frequently implemented by gas suppliers.

References

- EPA the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) Fact Sheet for Assessment Monitoring – Haloacetic Acid (HAA) (2016).
- 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).