Application Note

Environmental

Haloacetic Acid Analysis by the Agilent Intuvo 9000 Dual ECD System

Authors

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Abstract

In this application note, the analysis of haloacetic acid methyl esters was performed on the Agilent Intuvo 9000 Dual ECD system. Two Intuvo columns with different polarity were used for qualification and confirmation. Two types of carrier gases, nitrogen and helium, were used following the guidelines in the HJ 758-2015 standard and EPA 552.3 standard. The instrument performance including linearity, repeatability, and detection limits were evaluated on the haloacetic acid methyl esters standards. Finally, a set of 15 m analytical columns were applied for fast analysis purposes.

Introduction

Haloacetic acids (HAAs) in water are the by-products of chlorination disinfection of drinking water and are generated when chlorine reacts with organic matter in water. HAAs include several different compounds. Bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid are together referred to as HAA3. HAA5 is the sum of monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid. HAA3, HAA5, and bromochloroacetic acid together make up HAA9. The US Environment Protection Agency (EPA) regulates HAA5 and established the maximum contaminant level (MCL) of 60 µg/L for HAA5. In Europe, the European Parliament proposed a revision of the Drinking Water Directive defining the sum of HAA9 as 80 µg/L.[1] In China, the national standards of drinking water quality set the MCLs for dichloroacetic acid and trichloroacetic at 50 and 100 µg/L, respectively.

HAAs are acidic and hydrophilic compounds. Their concentration in water is usually quite low. For GC analysis, derivatization of the acids into methyl esters is required to generate good peak shapes and separation. An electron capture detector (ECD) is recommended in the China HJ 758-2015[2] and US EPA 552.3[3] methods, as this detector is selective for the detection of HAA methyl esters. The China HJ 758-2015 standard recommends HAA9 analysis in water using nitrogen as a carrier gas. Whereas EPA 552.3 guides the analysis of HAA9 and dalapon in drinking water using helium as a carrier gas. Both standards recommend dual columns with different polarity for HAA identity identification and confirmation.

In this application note, the Agilent Intuvo 9000 GC was used for HAA analysis. The unique Flow Chip design of Intuvo simplifies the setup of the analytical system with a single split/splitless inlet, dual columns, and dual ECDs. The test standards were commercial HAA methyl esters with surrogates included. The purpose of this work was to evaluate the Intuvo GC-ECD performance for HAA methyl esters analysis. The repeatability, linearity, and detection limits were investigated. Fast HAA methyl esters analysis was also performed with shorter analytical columns to increase the analysis speed.

Experimental

Instrument

The Intuvo 9000 GC system was equipped with one split/splitless inlet, one inlet splitter chip, dual nonidentical columns, and dual ECDs. The samples were injected using an Agilent 7650A automatic liquid sampler, evaporated in the heated inlet, and then carried to two analytical columns for separation followed by ECD detection. The sample was split equally between the qualification and confirmation columns. The GC analytical parameters and the consumables used are shown in Table 1 for both 30 and 15 m columns.

Chemical and standards

Stock solutions containing 100 mg/L of nine HAA methyl esters including dalapon and surrogate 2-bromobutyric acid methyl ester, the internal calibration standard of 1,2,3-trichloropropane (1,000 mg/L), and the dilution solvent, HPLC grade methyl *tert*-butyl ether (MTBE) were purchased from J&K Scientific (Beijing) Inc. HAA methyl esters working solutions were prepared by diluting the stock solutions to 1 mg/L with MTBE. The internal standard (IS) solution was diluted to 20 mg/L.

Table 1. Instrument conditions.

Intuvo 9000 GC-ECD Instrument Parameters			
Method Type		Method 1 for 30 m Intuvo column	Method 2 for 15 m Intuvo column
Autosampler		Agilent 7650A automatic liquid sampler	
Split/Splitless Inlet Mode		Splitless	Splitless
Inlet Temperature		210 °C	210 °C
Purge Flow		60 mL/min	60 mL/min
Purge Time		0.75 min	0.75 min
Intuvo Flow Path	Guard Chip	Track oven	Track oven
	Bus	270 °C	270 °C
Carrier Gas		Nitrogen/Helium	Nitrogen/Helium
Column Flow Rate		2 mL/min, constant flow	1.55 mL/min, constant flow
Oven Ramp Program		30 m columns: 40 °C, hold 5 min 2.5°C/min to 65 °C, 10°C/min to 85 °C, 20 °C/min to 205 °C, hold 2 min	15 m columns: 40 °C, hold 2.5 min 5 °C/min to 65 °C, 20 °C/min to 85 °C, 40 °C/min to 205 °C, hold 1 min
ECD Temperature		300 °C	
ECD Make Up Flow		30 mL/min, N_2 Column + make up = constant flow	
Inlet Liner		Agilent Ultra Inert, splitless liner with glass wool (p/n 5190-2293)	
Guard Chip		For split/splitless inlet (G4587-60565)	
Inlet Splitter		Flow Chip connecting Guard Chip and analytical columns (p/n G4588-60601)	
Columns		Column 1: Agilent J&W DB-5ms UI, 30 m × 0.25 mm, 0.25 µm (p/n 122-5522-UI-INT) Column 2: Agilent J&W DB-1701, 30 m × 0.25 mm, 0.25 µm (p/n 122-0732-INT)	Column 1: Agilent J&W DB-5ms UI, 15 m × 0.25 mm, 0.25 µm (p/n 122-5512UI-INT) Column 2: Agilent J&W DB-1701, 15 m × 0.25 mm, 0.25 µm (p/n 100-2111-INT)

Eight calibration levels were prepared by adding aliquots of the working solutions and internal standard to MTBE. The targeted concentrations were approximately 2, 5, 10, 20, 50, 100, 200, and 500 µg/L. The internal standard concentration was 500 µg/L.

Results and discussion

HAA methyl esters analysis on 30 m columns

The chromatograms of 50 µg/L HAA methyl esters produced using 30 m × 250 µm, 0.25 µm Agilent J&W DB-5ms and DB-1701 columns are shown in Figures 1 and 2. Figure 1 was obtained using Nitrogen as the carrier gas and Figure 2 was obtained using Helium as the carrier gas. All targeted analytes including the surrogate and internal calibration standard were well resolved. In the HJ758-2015 standard guidelines, the column dimension used for the collection of reference chromatograms was 30 m × 320 µm, 0.25 µm, and its phase ratio was 320. The reference chromatogram on the 5% phenyl-methylpolysiloxane column in HJ758-2015 showed poor resolution of trichloroacetic methyl ester, bromochloroacetic methyl ester, and the internal standard, with resolutions between each other less than 0.4.[2] The columns used in this work have thinner internal diameters and lower phase ratios, which results in better separation. In fact, baseline separation was achieved for the three compounds using the 250 µm DB-5ms column, as shown in Figures 1A and 2A.

The retention times (RTs) of HAA9 on the 30 m primary column (DB-1701) and the confirmation column (DB-5ms) with two carrier gases are tabulated in Table 2. It should be noted that the elution orders of DCAA/dalapon, BCAA/IS, DBAA/BDCAA were different on the two columns. RTs and area repeatability were evaluated by seven consecutive runs of the 50 µg/L calibrant. Using He as a carrier gas, the RT RSD% on the two columns was from 0.001 to 0.029%, with N_2 as carrier gas the RT precision was from 0.003 to 0.027% (Figure 3). Quantitation RSD% on the primary column was from 0.4 to 2.7% with He and from 0.5 to 2.0% with N_2 (Figure 4). The responses for individual compounds using N_2 as a carrier gas was generally 50 to 70% of that achieved with He as the carrier gas.

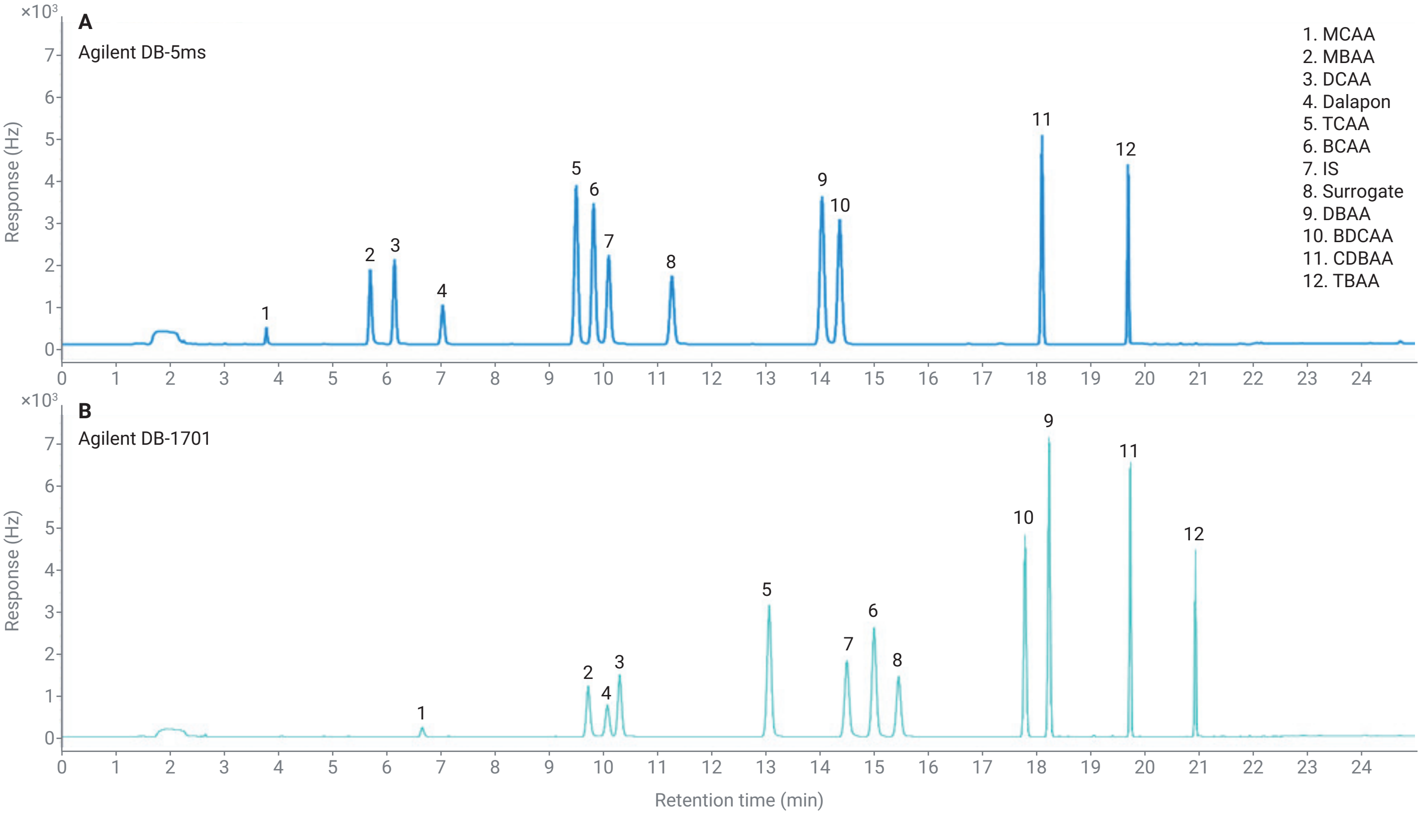


Figure 1. Chromatograms of 50 µg/L HAA methyl esters on 30 m Agilent J&W DB-5ms and DB-1701 Intuvo GC columns (N_2).

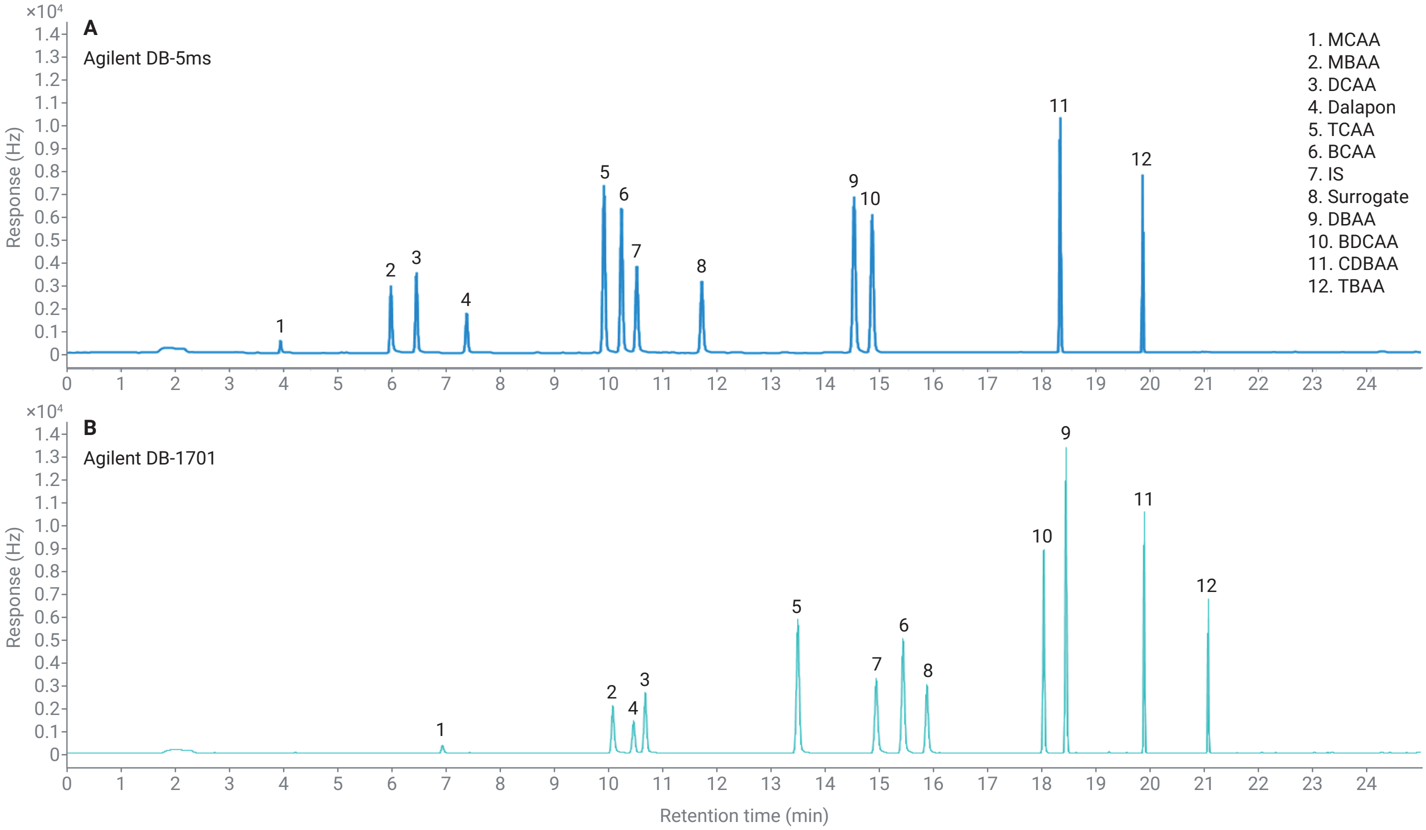


Figure 2. Chromatograms of 50 µg/L HAA methyl esters on 30 m Agilent J&W DB-5ms and DB-1701 Intuvo GC columns (He).

Table 2. RT and correlation coefficients of analyte calibration curves on 30 m columns with He and N_2 carrier gas.

Peak No.	Compound Name	RT (min) on 30 m Column				R^2		LOD (µg/L)	
		DB-1701 (N_2)	DB-1701 (He)	DB-5 (N_2)	DB-5 (He)	DB-1701 (N_2)	DB-1701 (He)	He	N_2
1	Monochloroacetic acid (MCAA)	6.655	6.922	3.77	3.941	0.996	0.996	0.664	1.200
2	Monobromoacetic acid (MBAA)	9.718	10.055	5.689	5.973	0.999	0.996	0.125	0.272
3	Dichloroacetic acid (DCAA)	10.299	10.652	6.134	6.443	0.998	0.997	0.094	0.216
4	Dalapon	10.073	10.437	7.023	7.367	0.998	0.996	0.169	0.398
5	Trichloroacetic acid (TCAA)	13.057	13.459	9.486	9.893	0.999	0.995	0.052	0.135
6	Bromochloroacetic acid (BCAA)	14.991	15.394	9.806	10.214	0.999	0.995	0.053	0.143
7	1,2,3 Trichloropropane (IS)	14.489	14.9	10.086	10.496	NA	NA		
8	2-bromobutanic acid (surrogate)	15.444	15.832	11.251	11.692	0.999	0.997	0.086	0.231
9	Dibromoacdtic acid (DBAA)	18.212	18.39	14.02	14.826	0.999	0.998	0.022	0.064
10	Bromodichloroacdetic acid (BDCAA)	17.769	17.981	14.346	14.492	0.997	0.998	0.050	0.129
11	Chlorodibromoacetic acid (CDBAA)	19.708	19.829	18.077	18.284	0.996	0.996	0.047	0.103
12	Tribromoacetic acid (TBAA)	20.909	21.006	19.664	19.801	0.995	0.995	0.072	0.136

The ECD linearity in the calibration range of 2 to 500 µg/L was evaluated at eight concentration levels. The concentration of the lowest calibration standard, 2 µg/L, was lower than the average MCL for a single haloacetic acid required by the USA EPA and China national standard. This means that the calibration range covered the concentration required to be detected by the regulations in the two regions. The calibration curves were developed on the primary column (DB-1701). All components have correlation coefficients (R^2) better than 0.995 for their linear curves (Table 2). The linearity results meet the requirement specified in the HJ758-2015 standard: R^2 no less than 0.995 in the calibration range of 10 to 200 µg/L.

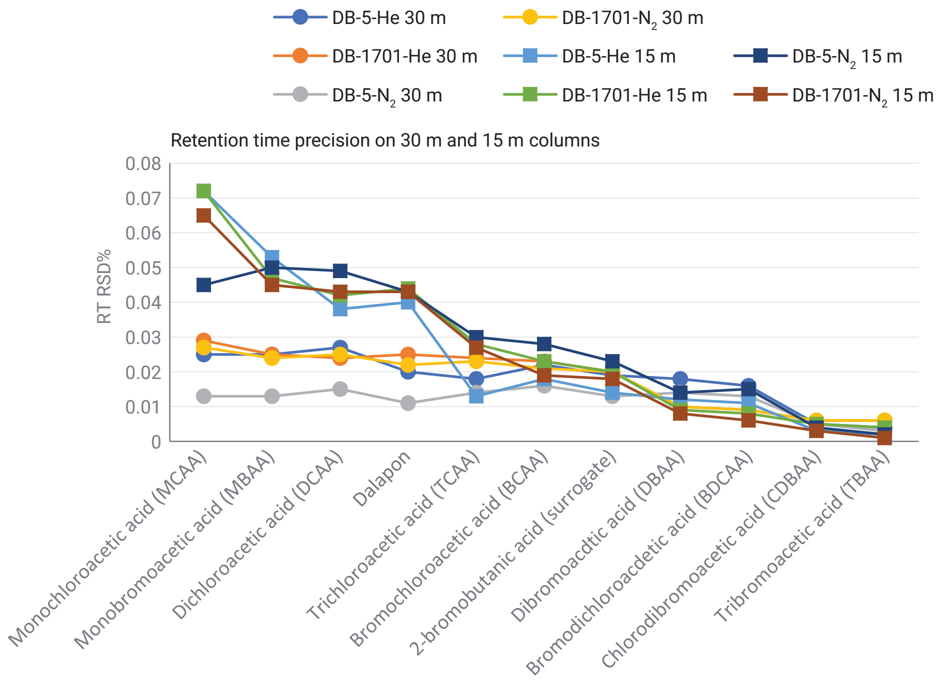


Figure 3. Retention time (RT) precision (RSD%) on 30 m (circles) and 15 m (squares) columns with He and N_2 as a carrier gases.

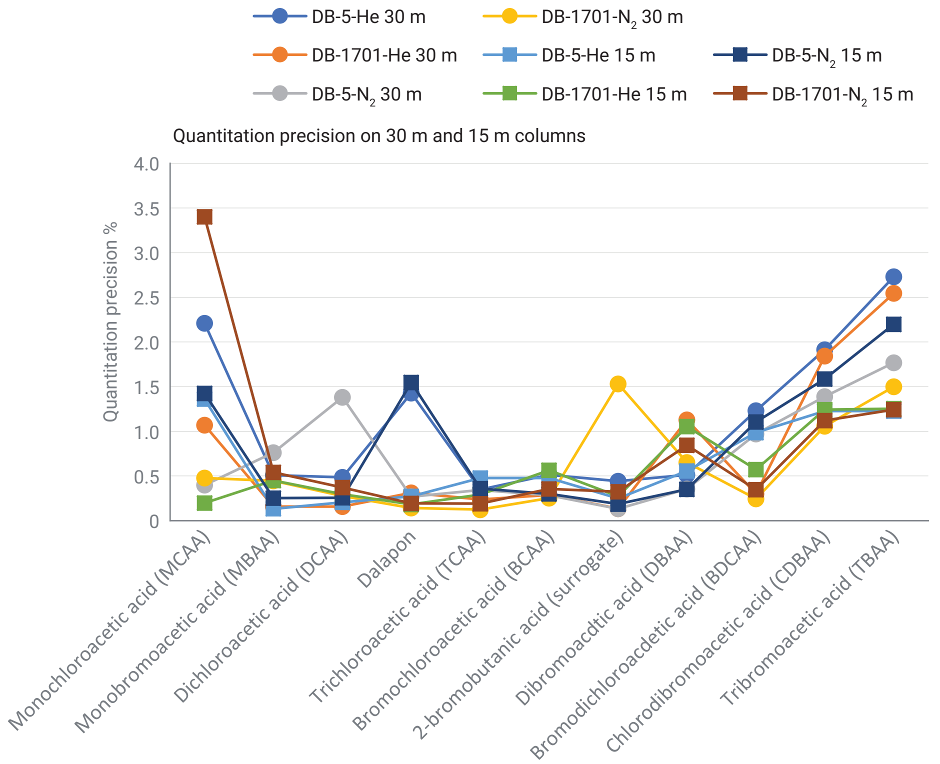
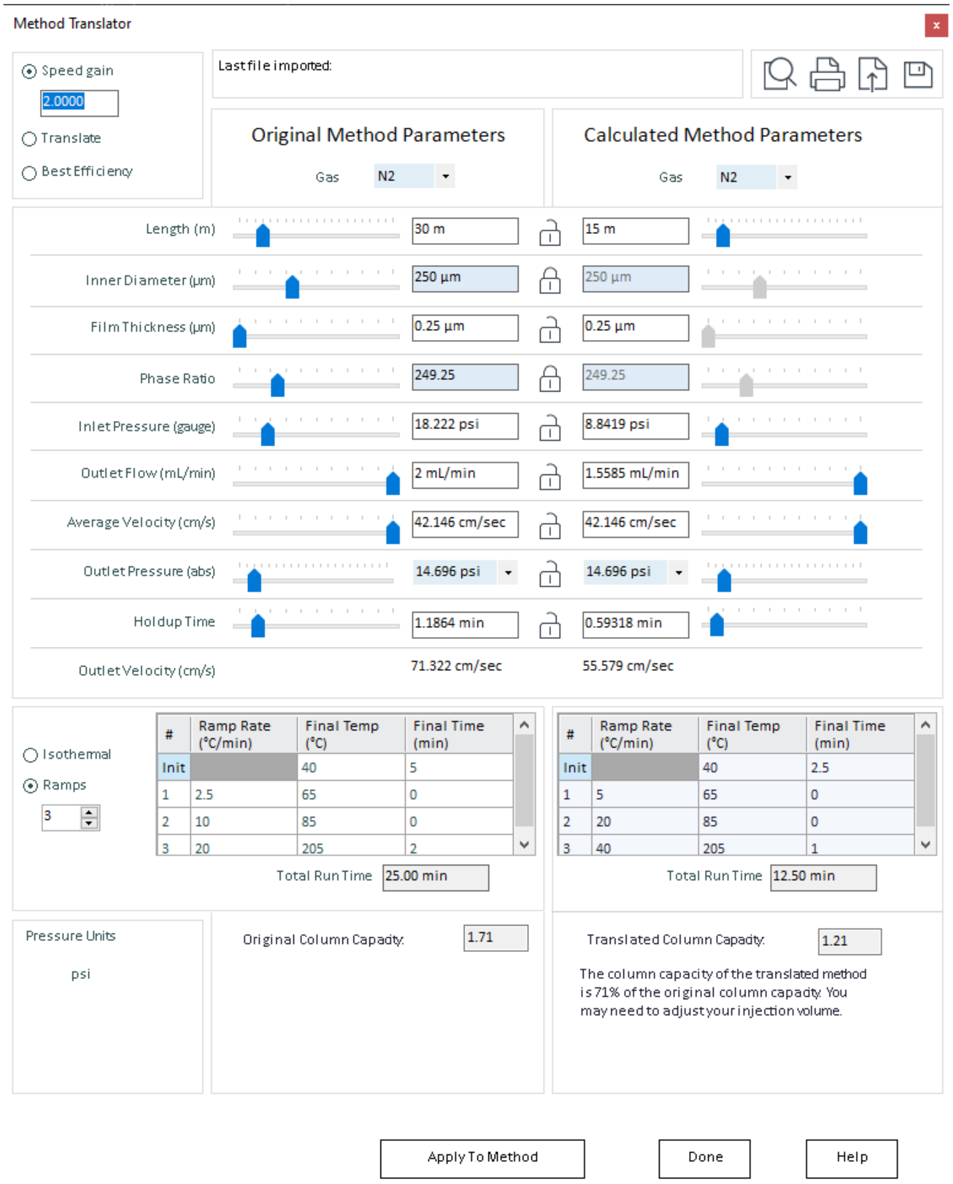


Figure 4. Quantitation precision (RSD%) on 30 m (circles) and 15 m (squares) columns with He and N_2 as carrier gases.

Fast analysis on 15 m columns

The chromatograms produced on 30 m columns showed adequate resolution of targeted compounds. To increase the analysis speed, 15 m columns with the same id and phase ratio were used for HAA methyl esters analysis. The method parameters on 15 m columns were developed using the method translation tool. With the desired speed gain set as 2.0, the parameters were generated in the method translator tool as shown in Figure 5, with N_2 carrier gas as an example. The column flow rates generated for He and Nitrogen were 1.538 and 1.558 mL/min, respectively. The following analysis used the faster rate. The chromatograms obtained on the 15 m columns are shown in Figures 6 and 7. All components are baseline separated except for dalapon and DCAA on the DB-1701 column, with a resolution of 1.3, which does not impact the identification and quantitation of both components considering their concentration in real samples are at the trace level. The RTs on the shorter column (shown in Table 3) were half of those on the 30 m column because the speed gain of 2.0 was set in the method translator tool. The analysis on 15 m columns was finished at approximately 10 minutes, resulting in an approximately 50% productivity improvement compared to performing the analysis on 30 m columns.



Method Translator

● Speed gain 2.0000
○ Translate
○ Best Efficiency

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	Original Method Parameters	Calculated Method Parameters
Gas	N2	N2
Length (m)	30 m	15 m
Inner Diameter (µm)	250 µm	250 µm
Film Thickness (µm)	0.25 µm	0.25 µm
Phase Ratio	249.25	249.25
Inlet Pressure (gauge)	18.222 psi	8.8419 psi
Outlet Flow (mL/min)	2 mL/min	1.5585 mL/min
Average Velocity (cm/s)	42.146 cm/sec	42.146 cm/sec
Outlet Pressure (abs)	14.696 psi	14.696 psi
Holdup Time	1.1864 min	0.59318 min
Outlet Velocity (cm/s)	71.322 cm/sec	55.579 cm/sec

○ Isothermal
● Ramps
3

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		40	5
1	2.5	65	0
2	10	85	0
3	20	205	2

Total Run Time 25.00 min

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		40	2.5
1	5	65	0
2	20	85	0
3	40	205	1

Total Run Time 12.50 min

Pressure Units psi

Original Column Capacity 1.71

Translated Column Capacity 1.21

The column capacity of the translated method is 71% of the original column capacity. You may need to adjust your injection volume.

Figure 5. Translation of the method on a 30 m column to a 15 m column (N_2).

Table 3. RT, correlation coefficients, and detection limits of analytes on 15 m columns with He and N_2 carrier gas.

Peak No.	Compounds Name	RT (min) on 15 m Column				R^2		LOD (µg/L)	
		DB-1701 (N_2)	DB-1701 (He)	DB-5 (N_2)	DB-5 (He)	DB-1701 (N_2)	DB-1701 (He)	He	N_2
1	Monochloroacetic acid (MCAA)	3.403	3.526	1.975	2.042	0.996	0.996	0.489	0.619
2	Monobromoacetic acid (MBAA)	4.92	5.086	2.916	3.041	0.999	0.998	0.106	0.140
3	Dichloroacetic acid (DCAA)	5.215	5.391	3.142	3.283	0.999	0.996	0.083	0.120
4	Dalapon	5.106	5.284	3.582	3.737	0.998	0.995	0.141	0.206
5	Trichloroacetic acid (TCAA)	6.593	6.796	4.803	4.993	0.999	0.998	0.046	0.070
6	Bromochloroacetic acid (BCAA)	7.553	7.759	4.96	5.157	0.999	0.999	0.048	0.081
7	1,2,3 Trichloropropane (IS)	7.304	7.516	5.098	5.296	NA	NA		
8	2-bromobutanic acid (surrogate)	7.781	7.98	5.677	5.888	0.998	0.997	0.076	0.134
9	Dibromoacdtic acid (DBAA)	8.964	9.074	7.053	7.282	0.999	0.998	0.021	0.037
10	Bromodichloroacdetic acid (BDCAA)	9.189	9.28	7.215	7.445	0.999	0.999	0.041	0.070
11	Chlorodibromoacetic acid (CDBAA)	9.952	10.013	9.093	9.194	0.998	0.998	0.037	0.056
12	Tribromoacetic acid (TBAA)	10.554	10.602	9.892	9.958	0.998	0.997	0.049	0.062

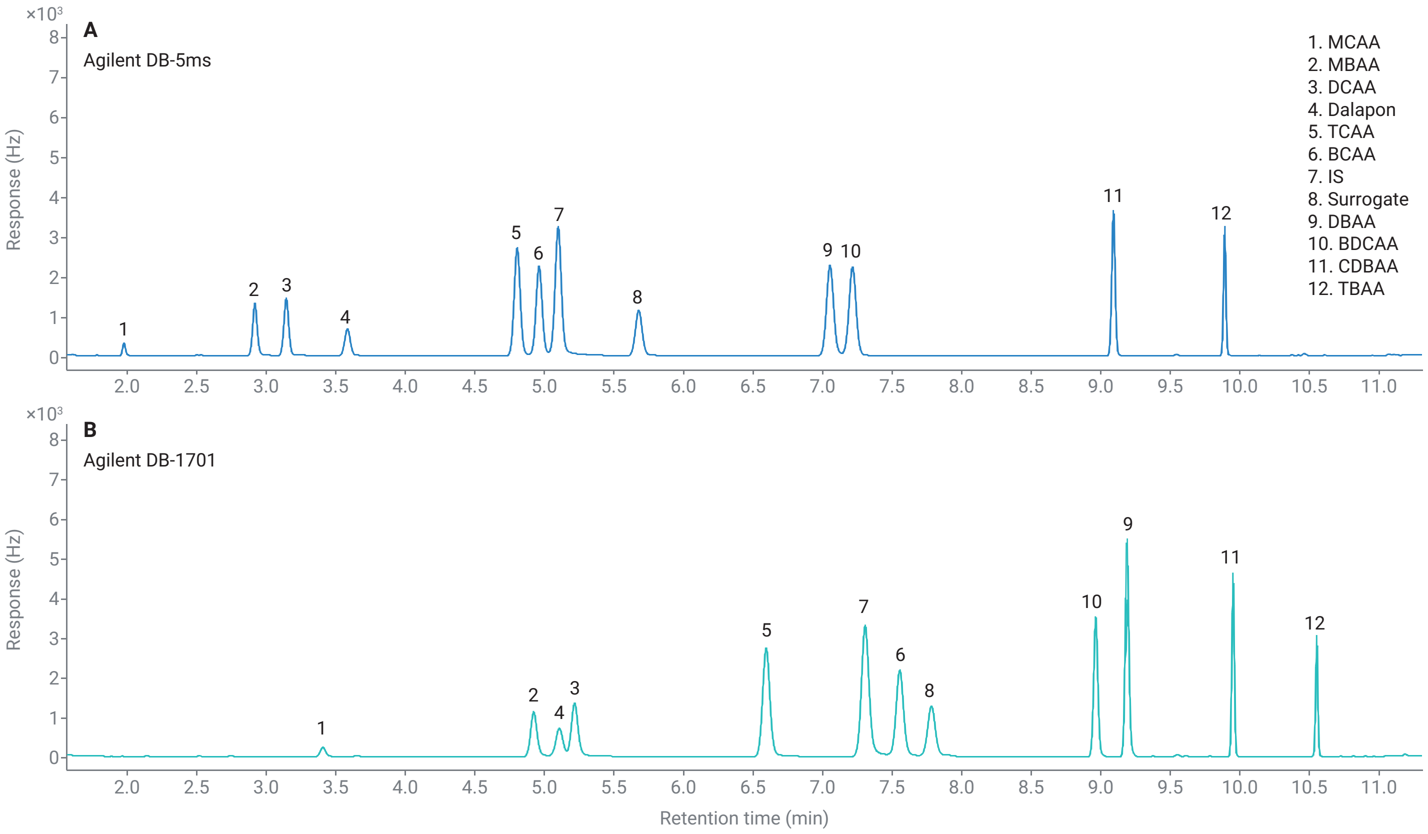

Figure 6. Chromatograms of 50 µg/L HAA methyl esters on 15 m Agilent DB-5ms and DB-1701 Intuvo GC columns (N_2).

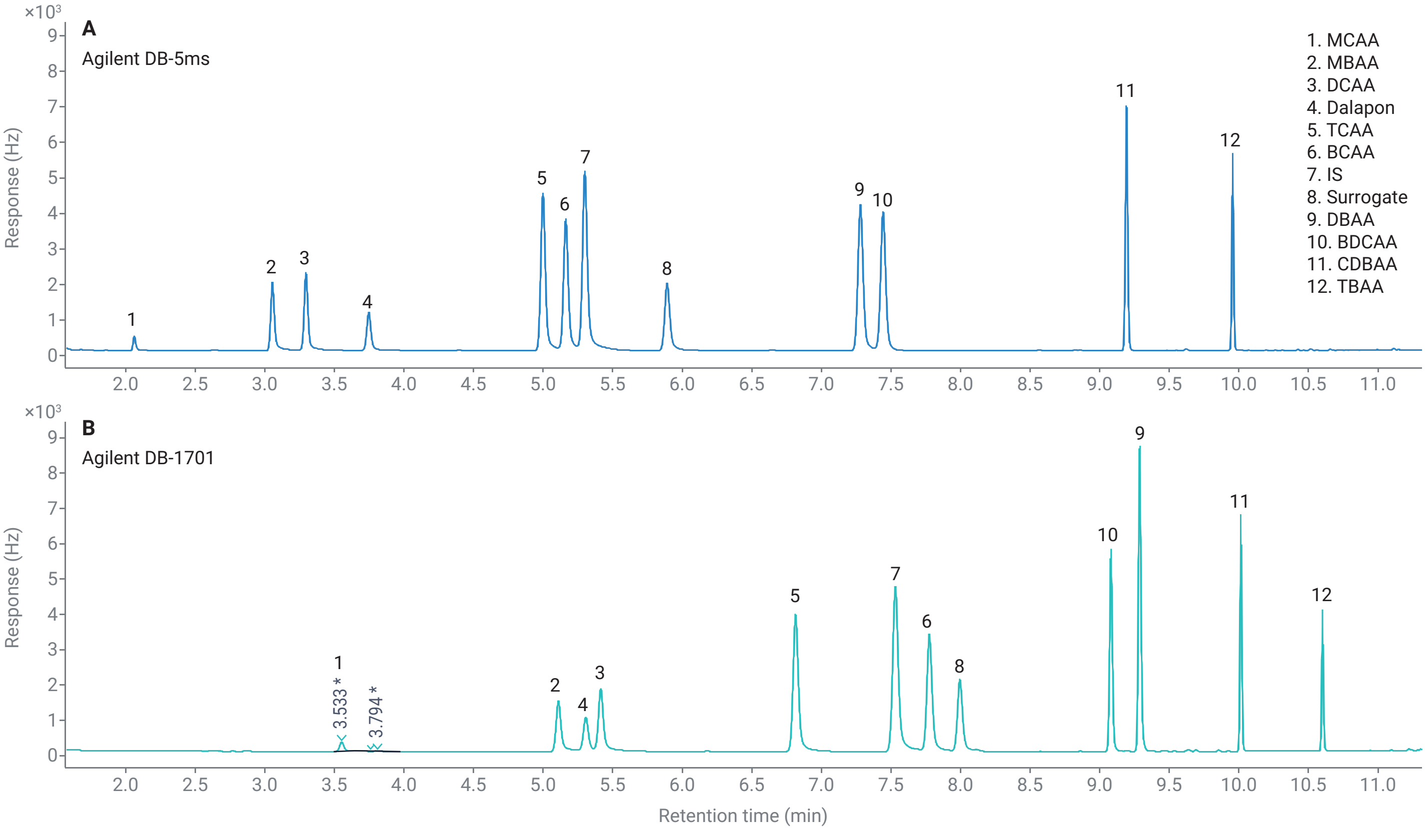

Figure 7. Chromatograms of 50 µg/L HAA methyl esters on 15 m Agilent J&W DB-5ms and DB-1701 Intuvo GC columns (He).

The repeatability was evaluated by seven injections of 50 µg/L calibrant. Using He as a carrier gas, the RT RSD% on the two columns was from 0.002 to 0.074%, with N_2 as the carrier gas the RT precision was from 0.001 to 0.065% (Figure 3). The first eluant MCAA had the biggest RT RSD% because its RT was the shortest and its RT standard deviation was similar to other components. Quantitation RSD% was from 0.3 to 1.3% with He and from 0.4 to 3.4% with N_2 (Figure 4). MCAA usually had the worst quantitation precision (2 to 3%) because its absolute response is much lower than other components.

The linearity was evaluated from 2 to 500 µg/L on the 15 m primary column (DB-1701). The linear curves of all components have correlation coefficients (R^2) better than 0.995. The detection limit of HAA9 methyl esters and dalapon on 15 and 30 m DB-1701 columns under different carrier gases were calculated at a signal-to-noise ratio (S/N) of 3 using the chromatograms of the 10 µg/L standard (Table 3). The detection limits on the 15 m columns were slightly better than those on 30 m columns. The detection limits using helium were better than those with nitrogen. For the real sample analysis, the HAAs need to be extracted from water and usually with 5 to 10 fold preconcentration, so the detection limit for real samples can be estimated to be lower than the instrument detection limit listed in the table.

Conclusion

The Agilent Intuvo 9000 Dual ECD system is a great choice for the analysis of HAA9 methyl esters and dalapon in water. The RT RSD% was from 0.001 to 0.07% and the quantitation precision was from 0.3 to 3.4%, proving good system repeatability. The detection limits obtained on 15 and 30 m column with Helium as carrier gas were comparable to each other, ranging from 0.02 to 0.67 µg/L. The detection limits with N_2 as carrier gas ranged from 0.04 to 1.2 µg/L and were higher than those obtained with He. Columns with different lengths can be used for targeted analysis and thus meet the different requirements on analysis speeds. The results show that the Agilent Intuvo 9000 Dual ECD system is a reliable platform for HAA methyl esters analysis, with easy setup, good reproducibility, and sensitive detection.

References

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