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Application News

No. GC-2004

Gas Chromatography

Fast Determination of Haloacetic Acids in Drinking Water According to EPA Method 552.3 using Rtx-CLPesticides Columns and 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]. EPA method 552.3[2] is approved for monitoring nine of the HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, CDBAA, TBAA) and dalapon in drinking water.

In this study, we showed that using Restek CLPesticides and CLPesticides2 columns with hydrogen carrier gas, the system met and exceeded EPA method 552.3 criteria. In addition, the GC run time is shortened by approximately 33% when compared to using the traditional 1701 and (5%-Phenyl)-methylpolysiloxane phase columns. Furthermore, the same setup can be used for organochlorine pesticides analysis, making it ideal for laboratories who would like the flexibility to use one system for multiple analyses.

■ 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	**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		

Dual column, one for primary determination and one for confirmation, is required by the EPA method 552.3 [2]. Normally, a column with 1701 phase was used as the primary column and a column with (5%-Phenyl)-methylpolysiloxane phase was used as the confirmation column. And traditionally, helium (He) is used as the carrier gas for this method. We previously assayed HAA9 using Rtx-1701 and Rxi5Sil-MS with hydrogen (H_2) carrier gas and demonstrated H_2 as a cost-effective alternative carrier gas [3]. The last HAA compound (TBAA) elutes around 25-27 min on both columns with either He or H_2 carrier gas. To minimize operational expenses and increase throughput, we explored alternative system configurations to shorten the GC run time while maintaining adherence to EPA's requirements in method 552.3.

In this application, we investigated using Restek Rtx-CLPesticides (Rtx-CLP) as the primary column and Rtx-CLPesticides2 (Rtx-CLP2) as the confirmation column to determine HAAs concentrations with H_2 carrier gas according to EPA 552.3. These columns were originally developed for the analysis of organochlorine pesticides and herbicides. We analyzed organochlorine pesticides on Rtx-CLPesticides column as well to evaluate the suitability of the same system for multiple environmental analyses.

■ 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) and Organochlorine Pesticide Mix AB #1 (20 components, Cat. No. 32291) 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 a 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 an internal standard was run on the GC system. The concentration indicated in Results and Discussion represents 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.

■ Results and Discussion

Previously, we demonstrated successful analysis of methylated HAA9, dalapon and surrogate simultaneously on Rtx-1701 and Rxi5Sil-MS (EPA column set) according to the EPA 552.3 method using Shimadzu's GC-2030 with dual inlet, detector and autosampler with He or H_2 carrier gas [3]. The last HAA compound eluted around 25-27min on both columns. In this application, we sought to improve this method by using an alternative column set, Rtx-CLPand Rtx-CLP2 (CLP column set), to determine HAAs and dalapon concentrations according to EPA 552.3 method criteria.

Comparison of CLP Column Set to EPA Column Set

The chromatograms obtained with H_2 carrier gas run on Rtx-CLP and Rtx-CLP2 were compared to those run on Rtx-1701 and Rxi5Sil-MS. The retention times of each compound on different columns are shown in Table 3. The retention times of the last eluting HAA compound, TBAA, on the CLP column set are 15 and 16 min, versus 27 and 26 min on the EPA column set, a savings of over 1/3 the analysis time on each column.

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-CLPesticides, 30m x 0.32mm x 0.32µm (primary) Rtx-CLPesticides2, 30m x 0.32mm x 0.25µm (confirmation)
Injector Mode	Split at 1:1 ratio increase to 10 after 0.5min
Injection Volume	1.0 µL
Carrier Gas	Hydrogen
Flow mode	Constant initial linear velocity of 25cm/sec
Column Temp	35°C, 4min – 10°C/min – 250°C, 1min
Injection Port Temp	250°C
Detector Temp and Current	300°C, 2nA
Detector Gases	N_2 15mL/min, with Detector Constant Flow Mode

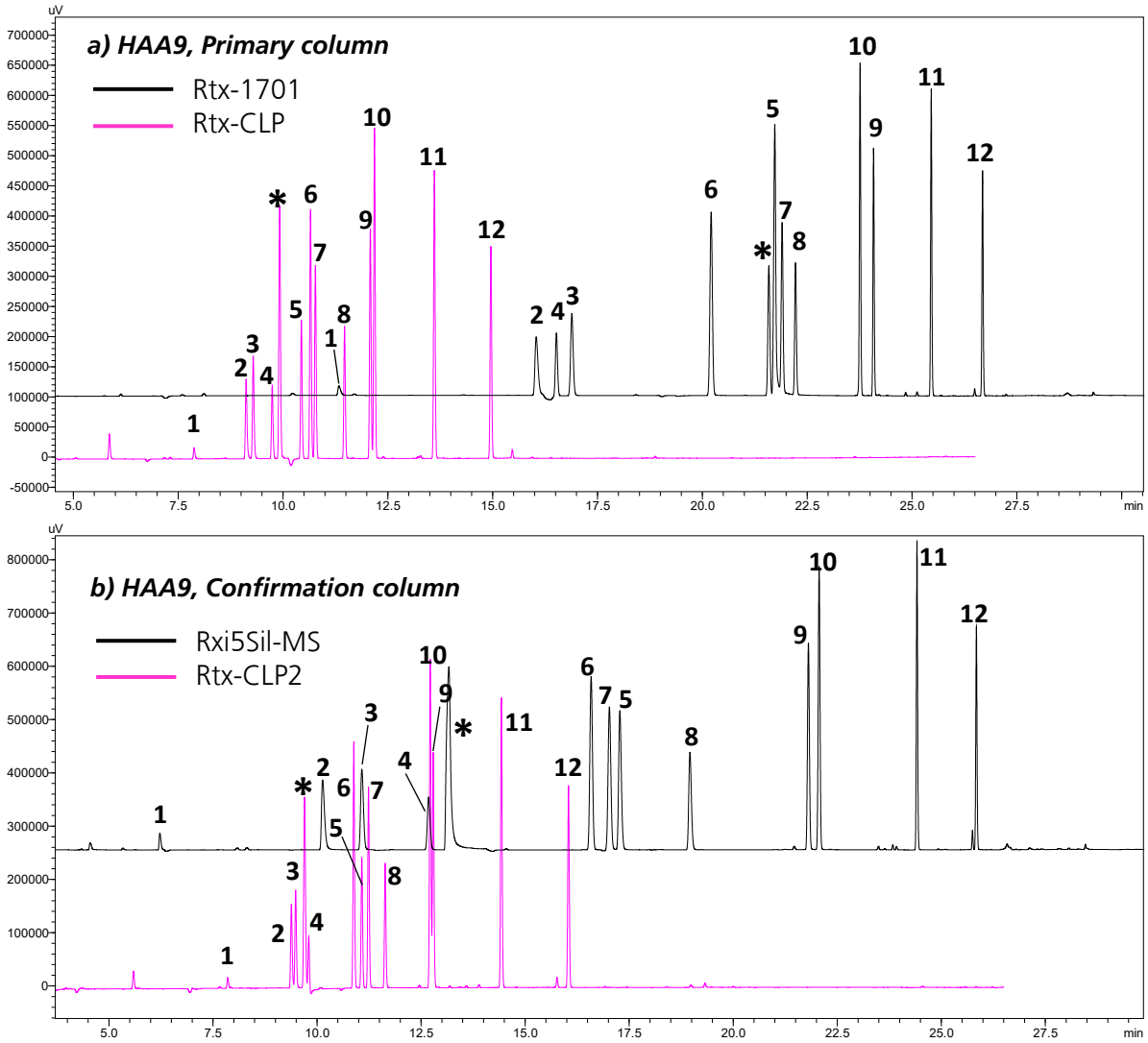


Figure 1: Chromatograms of 10 ppb HAA Methyl Ester Mix analyzed on indicated a) primary and b) confirmation column. Peaks indicated with an asterisk do not correspond to any of target peaks.

Table 3: List of compounds analyzed and the retention times with H_2 carrier gas.

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

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.

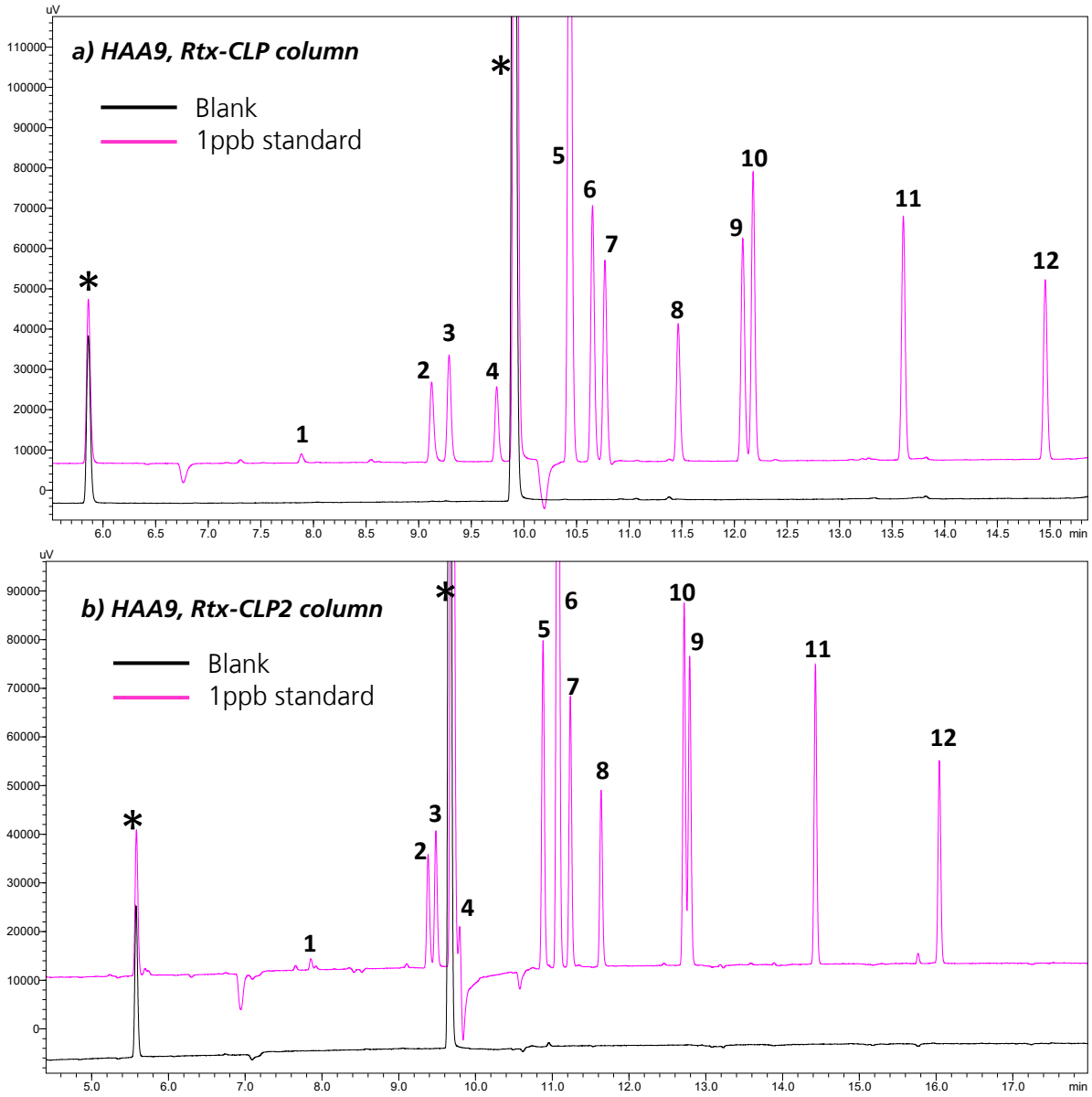


Figure 2: Chromatograms of MTBE blanks and 1 ppb HAA Methyl Ester Mix on a) primary column (Rtx-CLP) and b) confirmation column (Rtx-CLP2) using H_2 carrier gas. Peaks indicated with an asterisk do not correspond to any of target peaks.

Calibration Curves with H_2 Carrier Gas

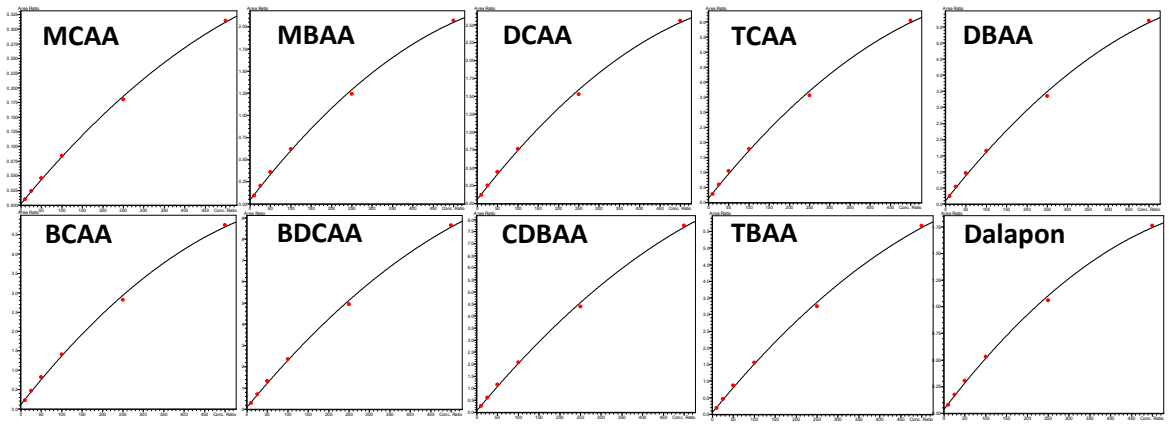
The HAA methyl ester mix was diluted to prepare a six-point calibration curve with concentrations from 1 to 50 ppb in water. Internal standard calibrations fitted quadratically with 1/A weighting without forcing through zero were built for all targets. The calibration curves and the coefficients of determination (r^2 Values) are shown in Figure 3 and Table 4. All r^2 values were higher than 0.995.

The method requires demonstration of calibration accuracy. Specifically, the analyte concentrations should be within ±30% of the expected values, except for the 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).

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

Compounds	r^2 Values	
	Rtx-CLP	Rtx-CLP2
MCAA	0.999	0.999
MBAA	0.998	0.998
DCAA	0.998	0.998
TCAA	0.998	0.998
DBAA	0.998	0.998
BCAA	0.998	0.998
BDCAA	0.998	0.998
CDBAA	0.999	0.999
TBAA	0.998	0.999
Dalapon	0.998	0.998

a) Rtx-CLP



b) Rtx-CLP2

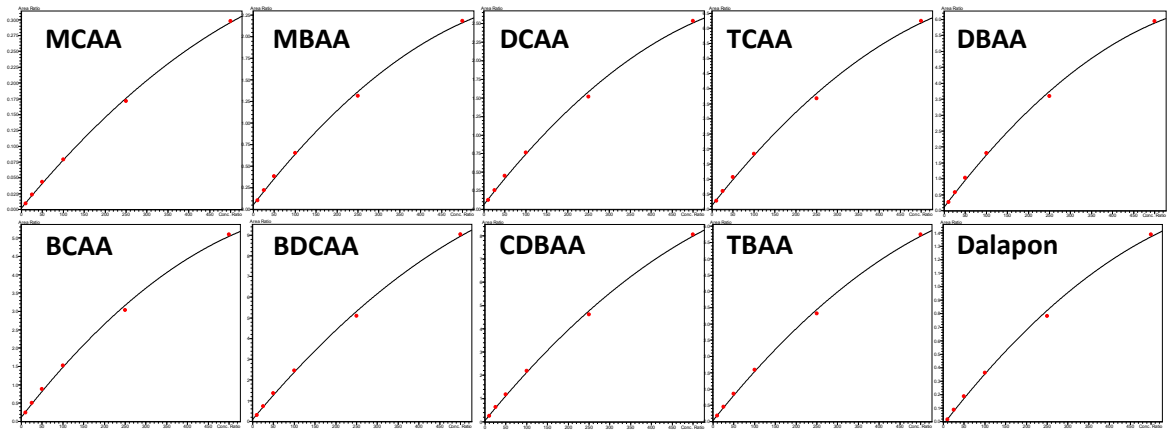


Figure 3. Six-point calibration curves for HAA9 and Dalapon on a) primary column (Rtx-CLP) and b) confirmation column (Rtx-CLP2) using H_2 carrier gas.

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 differences were < ±21% for the lowest calibration level and < ±10% for all other levels.

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	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

Analysis of Halogenated Pesticides using the Rtx-CLPesticides Column

To confirm that other contaminants can be succesfully analyzed using the Shimadzu GC-ECD-exceed and Rtx-CLP column, a mix of 20 organochlorine pesticides was assayed.

According to the EPA criteria listed in EPA method 608/8081B, resolution is acceptable if the valley height between two peaks is less than 40% of the height of the smaller peak. As shown in Figure 4, all 20 compounds were resolved in just over 5 min

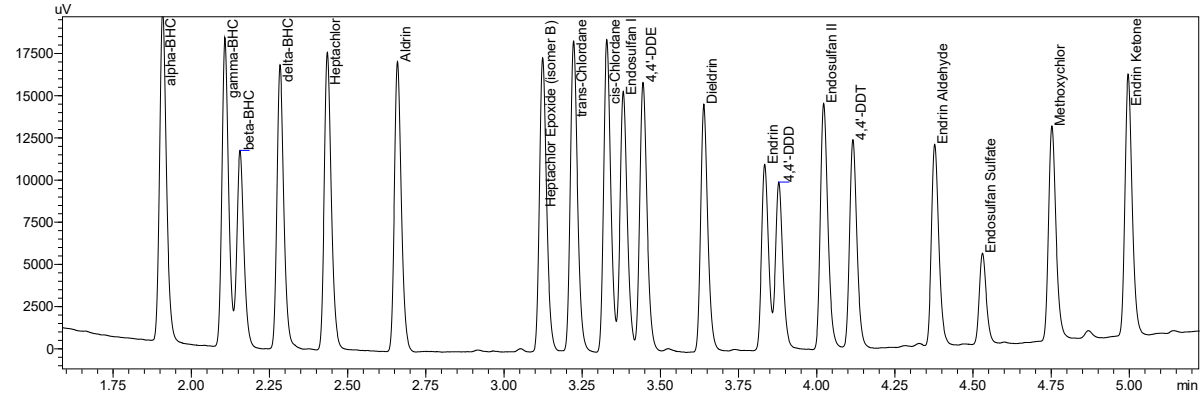


Figure 4: Chromatogram of 4 ppb organochlorine pesticides standard in hexane analyzed on Rtx-CLP column using He carrier gas.

■ Conclusion

CLP column set was used successfully to analyze HAA9 compounds according to EPA method 552.3 on Nexis GC-2030 with dual line split/splitless injectors and ECD-exceeds. The results obtained met and exceeded EPA's quality assurance requirements for HAA9 and dalapon, proving that CLP column set is a suitable alternative column set for this method.

The use of this column set reduces run time by approximately 33%. Consequently, operating cost for the laboratory decreases and the sample throughput can be increased. Moreover, same GC set up can be used to perform additional EPA methods, such as the analysis of organochlorine pesticides in environmental samples.

■ 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)
3. Determination of Haloacetic Acids in Drinking Water According to EPA Method 552.3 using Hydrogen Carrier Gas, Shimadzu Application News GC-2002 (2020)
4. EPA method 608.3, Organochlorine Pesticides and PCBs by GC/HSD, EPA-821-R-14-016 (2014)
5. SW-846 Test Method 8081B, Organochlorine Pesticides by Gas Chromatography, EPA (2007)

■ 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	
227-36266-01	SH-Rtx-CLP Capillary Column, 0.32 x 0.32 x 30	each	Column (primary)
227-36267-01	SH-Rtx-CLP2 Capillary Column, 0.32 x 0.25 x 30	each	Column (confirmation)

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