Chlorinated Solvents and Disinfection By-Product Analysis Using Agilent J&W HP-1ms Ultra Inert and DB-1301 Capillary GC Columns

Application Note

Environmental

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Abstract

Trace-level chlorinated hydrocarbon analyses using methods such as US EPA Method 551.1 are important tools for assessing organochlorine contamination in water. The wide diversity of target organochlorine compounds can prove chromatographically challenging due mainly to their high volatility and limited retention. This application note shows the benefits of using an Agilent J&W HP-1ms Ultra Inert Capillary GC column as the primary column for detection in this dual-column analysis.

Agilent Technologies

Introduction

The disinfection of water for safe human consumption is a critical process worldwide. Chlorination is an effective means of achieving water disinfection, but has been shown to produce a wide variety of disinfection byproducts (DBPs). These byproducts are formed when the chlorinated disinfectant reacts with naturally present organic matter. Some of the byproducts formed include trihalomethanes, haloacetonitriles, and chloropropanones. Many of the DBPs have been linked to adverse health effects, including birth defects, bladder and colon cancer [1–3]. Because of these health concerns, the levels of the by-products are monitored to ensure they are below safety standard limits.

US EPA Method 551.1 [4] is a commonly used method for detecting organochlorine compounds in water samples by GC/ECD. This method encompasses several classes of analytes: chlorinated organic solvents, trihalomethanes (THMs), haloacetonitriles, and other DBPs. The high volatility and limited retention of several of these analytes can prove problematic chromatographically. Reliable detection at very low levels is also a challenge for this analyte set. Active sites in the sample path can compromise an analyte's response. Minimizing activity in the GC column is essential to ensure accurate quantitation. Capillary GC column activity as a potential source of result uncertainty has been effectively eliminated with the Agilent J&W Ultra Inert series of columns.

Agilent Technologies, Inc. has implemented new testing procedures for the J&W Ultra Inert column series to more effectively evaluate GC column inertness performance. This testing procedure employs deliberately aggressive probes to thoroughly investigate column inertness performance on this new series of columns. These aggressive probes, including 1-propionic acid, 4-picoline, and trimethyl phosphate, are used to verify each column's inertness performance.

A standard preparation containing chlorinated solvents, THMs, and disinfection by-products (DBPs) was analyzed to evaluate column performance. This analysis used simultaneous primary and confirmation analysis from a single injection source through an Agilent Capillary Flow Technology two-way splitter without makeup device. The primary analysis column used was an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm and the confirmation column was an Agilent J&W DB-1301 30 m × 0.25 mm × 1.0 µm.

Experimental

An Agilent 7890A GC equipped with dual µECDs and an Agilent 7683B automatic liquid sampler was used for this series of experiments. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow path consumable supplies used in these experiments.

Table 1. Chromatographic Conditions for EPA Method 551.1 Calibration Standards

GC:	Agilent 7890A
Sampler:	Agilent 7683B, 5.0 µL syringe (Agilent p/n 5181-1273) 0.5 µL splitless injection
Carrier:	Helium 25 cm/s, constant flow
Inlet:	Splitless; 200 °C, Purge flow 20 mL/min at 0.25 min
Inlet liner:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Retention gap:	1 m 0.32 mm id deactivated fused silica high-temperature tubing (Agilent p/n 160-2855-5)
Column 1:	Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm (Agilent p/n 19091S-733UI)
Column 2:	Agilent J &W DB-1301 30 m × 0.25 mm × 1.0 µm (Agilent p/n 122-1333)
Oven:	33 °C (14 min) to 60 °C (5 °C/min), hold 5 min, 15 °C/min to 275 °C, hold 20 min
Detection:	Dual G2397A µECD; 300 °C, const col + makeup (N_2) = 30 mL/min

Table 2 Flow Path Supplies

CFT device:	Two-way splitter accessory without makeup gas (Agilent p/n G3181B)
	Alternative: Deactivated quartz y-splitter (Agilent p/n 5181-3398)
CFT fittings:	Internal nut (Agilent p/n G2855-20530)
	Swaging nut (Agilent p/n G2855-20555)
CFT ferrules:	SilTite ferrules, 0.32 mm id (Agilent p/n 5188-5362)
	SilTite ferrules, 0.25 mm id (Agilent p/n 5188-5361)
Vials:	Amber crimp cap glass vials (Agilent p/n 5183-4496)
Vial caps:	Crimp caps (Agilent p/n 5282-1210)
Vial inserts:	100 µL glass/polymer feet (Agilent p/n 5181-8872)
Syringe:	5 µL (Agilent p/n 5181-1273)
Septum:	Advanced Green (Agilent p/n 5183-4759)
Inlet liners:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Ferrules:	0.4 mm id short; 85/15 Vespel/graphite (Agilent p/n 5181-3323)
	0.5 mm id short; 85/15 Vespel/graphite (Agilent p/n 5062-3514)
20x magnifier:	20x magnifier Agilent p/n 430-1020)

Sample Preparation

EPA551.1 Standards

Two EPA551.1 standards containing chlorinated solvents, THMs, and DBPs were purchased from AccuStandard (New Haven, CT) and used to prepare a six-level calibration standard set. The stock solutions as delivered had a nominal concentration of 1000 µg/mL. The calibration standards were prepared at standard concentrations of 0.1, 0.05, 0.02, 0.01, 0.005, and 0.002 µg/mL. All solutions were prepared in MTBE using class A volumetric pipettes and flasks. MTBE used was Burdick and Jackson high-purity grade purchased thorough VWR International (West Chester, PA). MTBE was used as a reagent blank and syringe wash solvent.

Column Installation Using Two-Way Splitter Without Makeup Gas Capillary Flow Technology (CFT)

This analysis was performed using simultaneous confirmation from a single injector onto both the primary and confirmation columns. While a typical injector setup for dual column analysis uses a deactivated glass or quartz Y-splitter (Agilent p/n 5181-3398) to join the retention gap to the primary and confirmation columns, an Agilent Capillary Flow Technology two-way splitter without makeup gas (p/n G3181B) was employed. This device holds several advantages over the Y-splitter.

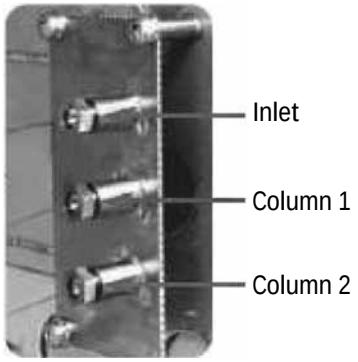
Correct assembly of a Y-splitter can be difficult, and detachment and/or leaks may occur upon thermal cycling of the oven. When using the Y-splitter, a periodic check of the connections is recommended. The Agilent CFT splitter uses SilTite metal ferrules that minimize the likelihood of leaks or detachment, even with thermal cycling as high as 350 °C. Installation of the retention gap and columns into the splitter module uses ferrules and internal nuts similar to a typical column installation. The CFT splitter is deactivated, yielding an inert sample path. The point-of-seal of the fittings design provides extremely low dead-volume column connections, improving optimal performance.

For this analysis, a 1 m, 0.32 mm id deactivated fused silica high-temperature tubing was installed into the inlet and into the top position of the two-way splitter. For the column connections to the splitter, the column end was threaded though the internal nut, SilTite ferrule, and swaging nut. The swaging nut was then tightened, seating the ferrule onto the column. Using a column cutter, the column end was trimmed to about 0.3 mm of column extending above the ferrule. The column was then connected to the two-way splitter. A diagram of the splitter and column setup is shown in Figure 1. Because the column connections are individually installed in the splitter, column maintenance can be done independent of the other column.

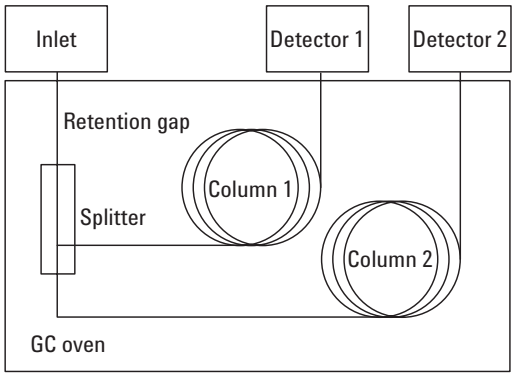
Results and Discussion

Baseline Inertness Profile for Ultra Inert Columns

The basic approach for inertness verification for the Agilent J&W Ultra Inert series of capillary GC columns is QC testing with aggressive active probes at low concentration and low temperature [5]. This is a rigorous approach that establishes



Two-way splitter without makeup gas connections



Plumbing diagram for the two-way splitter without makeup gas

Figure 1. Agilent Capillary Flow Technology two-way splitter without makeup gas (p/n G3181B) and diagram of instrument setup of simultaneous confirmation from a single injection onto both the primary and confirmation columns.

consistent baseline inertness profiles for each column. The baseline inertness profile then serves as a predictor for successful analysis of chemically active species that tend to adsorb onto active sites, particularly at trace level like the chlorinated species in this application example. Additional application examples can be found in references [6–10].

EPA 551.1 Analysis

In this application note a six-level calibration curve set was evaluated over the concentration range of 0.002 to 0.1 µg/mL using simultaneous confirmation of a single injection. A two-way splitter without makeup capillary flow device (p/n G3181B) was used in place of a y-splitter to split the sample onto the two columns. Figure 2 shows a chromatogram for the 5 pg on column loading from a single injection of the 551.1 standard on the primary and confirmation columns.

Excellent peak resolution and peak shape were obtained on both the J&W HP-1ms Ultra Inert and the J&W DB-1301 columns as shown in Figures 3 and 4. Chloral hydrate is unstable and, as is described in the EPA method, does not resolve as a discreet peak due to selectivity on a 1301 phase column. Figure 5 shows that chloral hydrate is well resolved and has symmetrical peak shape even at low levels on the J&W HP-1ms Ultra Inert primary column. One method criteria for primary column performance for this analysis is the resolution between bromodichloromethane and trichloroethylene. The acceptance criteria requires a resolution greater than 0.5 using the calculation described in the method. Figure 6 shows the resolution of bromodichloromethane and trichloroethylene in the 0.05 µg/mL EPA 551.1 standard on the J&W HP-1ms Ultra Inert primary analysis column. The resolution was found to be 0.787, well above the method criteria. This resolution was also determined at the lowest and highest level standards studied in this application. The resolution was 0.825 for the 0.002 µg/mL standard (0.5 pg on column) and 0.734 for the 0.1 µg/mL standard (25 pg on column) as can be seen in Figure 7.

Linearity was excellent across the range studied, giving R^2 values of 0.998 or greater for the chlorinated analytes on both the J&W HP-1ms Ultra Inert primary analysis column and also on the J&W DB-1301 confirmation column. Table 3 indicates the correlation coefficients for each component on both columns.

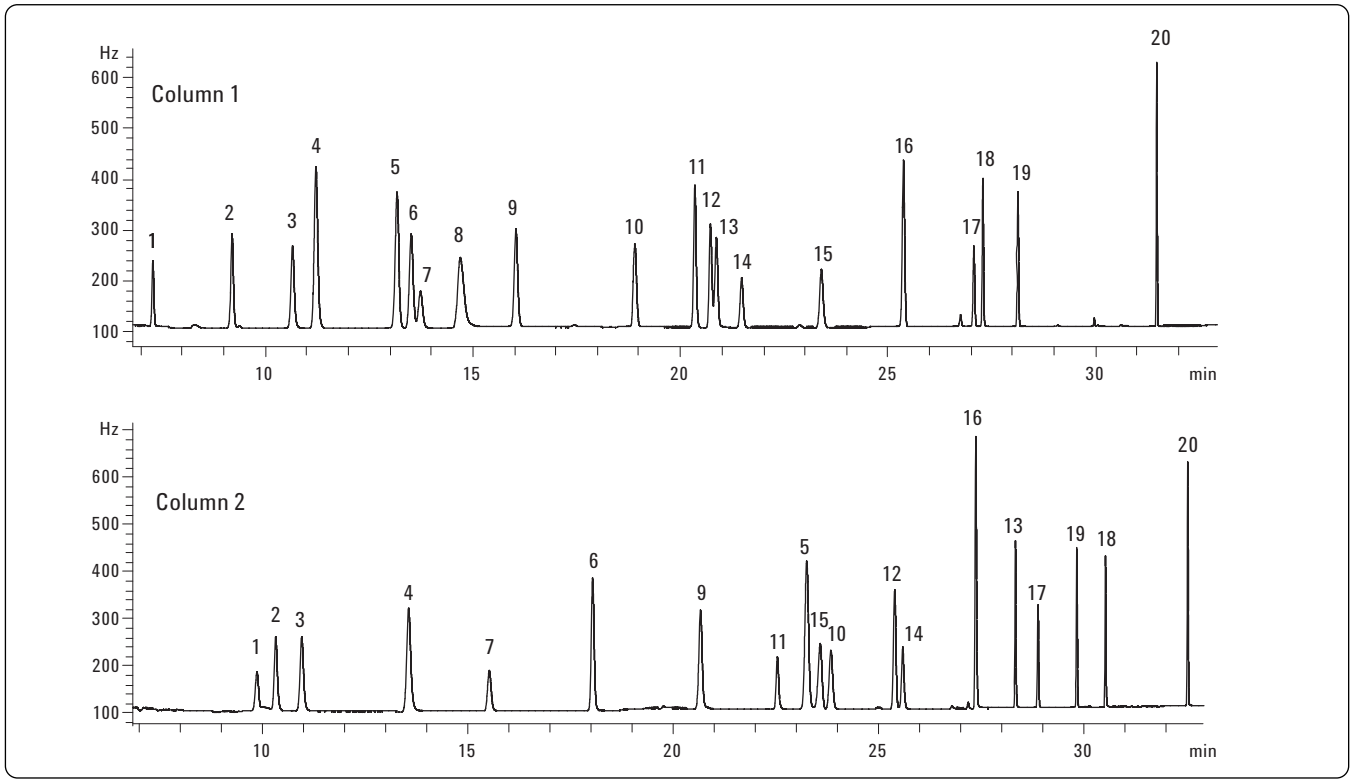


Figure 2. Single-injection chromatogram of the 5 pg on-column EPA551.1 standard solution loading on an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm capillary GC column (p/n 19091S-733UI) and J&W DB-1301 30 m × 0.25 mm × 1.0 µm capillary GC column (p/n 122-1333). Chromatographic conditions are listed in Table 1. Refer to Table 4 for a peak number key.

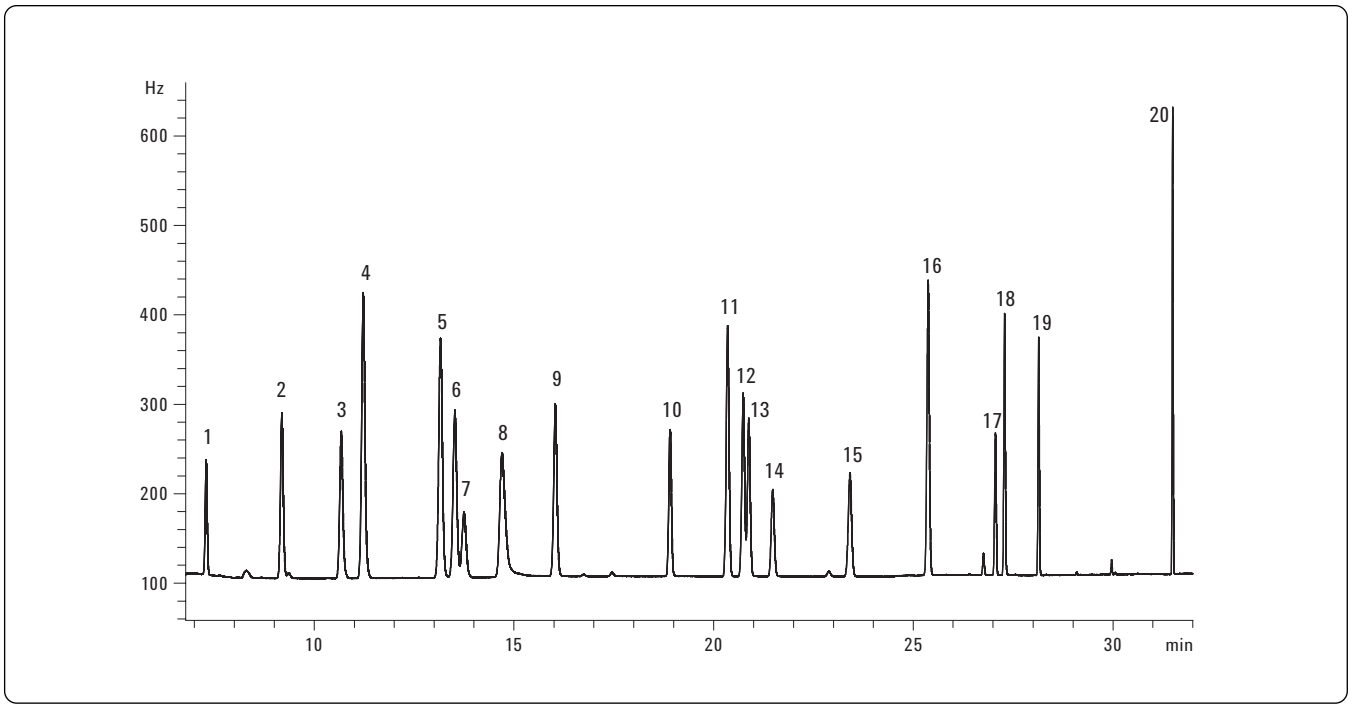


Figure 3. Enlarged chromatogram of the 5 pg on-column EPA551.1 standard solution loading on an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm capillary GC column (p/n 19091S-733UI). Chromatographic conditions are listed in Table 1. Refer to Table 4 for a peak number key.

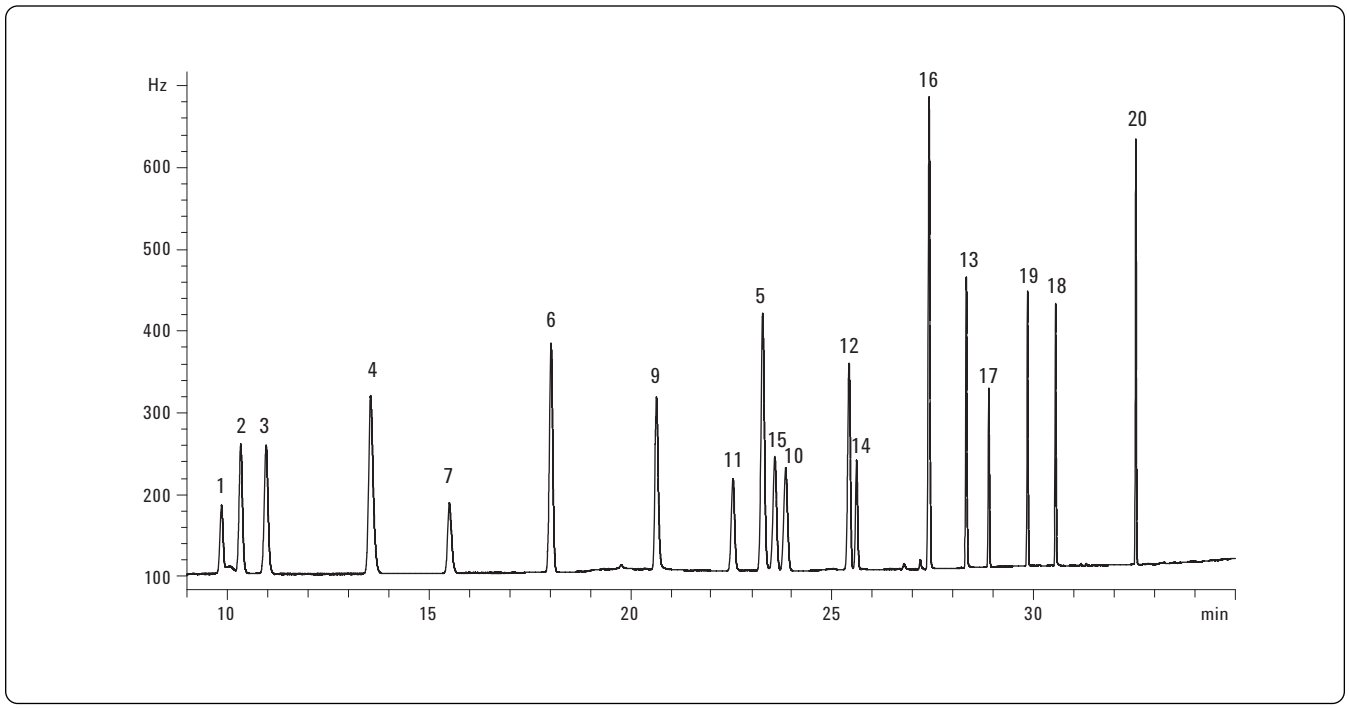


Figure 4. Enlarged chromatogram of the 5 pg on-column EPA551.1 standard solution loading on an Agilent J&W DB-1301 30 m × 0.25 mm × 1.0 µm capillary GC column (p/n 122-1333). Chloral hydrate (peak # 8) does not elute as a discreet peak on this column. Chromatographic conditions are listed in Table 1. Refer to Table 4 for a peak number key.

Table 3. Correlation Coefficients for the Analytes in the EPA Method 551.1 Standard Over the 0.002 to 0.1 µg/mL Range of This Study for a 0.5 µL Single Injection Loading onto the Dual Column System

Component	Agilent J&W HP-1ms UI R^2	Agilent J&W DB-1301 R^2
Chloroform	0.9997	0.9997
1,1,1-Trichloroethane	0.9999	0.9999
Carbon tetrachloride	0.9987	0.9988
Trichloroacetonitrile	0.9989	0.9979
Dichloroacetonitrile	0.9995	0.9993
Bromodichloromethane	0.9995	0.9994
Trichloroethylene	0.9998	0.9998
Chloral hydrate	0.9982	X
1,1-Dichloro-2-propanone	0.9999	0.9995
1,1,2-Trichloroethane	0.9998	0.9994
Chloropicrin	0.9995	0.9975
Dibromochloromethane	0.9995	0.9994
Bromochloroacetonitrile	0.9993	0.9981
1,2-Dibromoethane	0.9998	0.9999
Tetrachloroethlyene	0.9994	0.9999
1,1,1-Trichloro-2-propanone	0.9995	0.9992
Bromoform	1.0000	0.9998
Dibromoacetonitrile	0.9984	0.9975
1,2,3-Trichloropropane	0.9999	1.0000
1,2-Dibromo-3-chloropropane	0.9995	0.9998

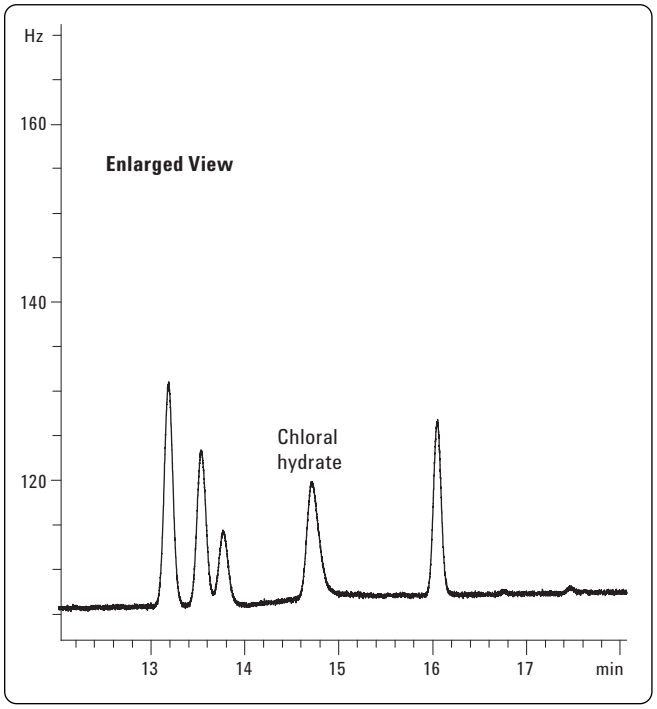


Figure 5. Enlarged chromatogram for a 0.5 µL injection of 0.002 µg/mL EPA 551.1 standard on the Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm capillary GC column. Peak shape on the J&W HP-1ms Ultra Inert column is symmetrical and well resolved from the other components.

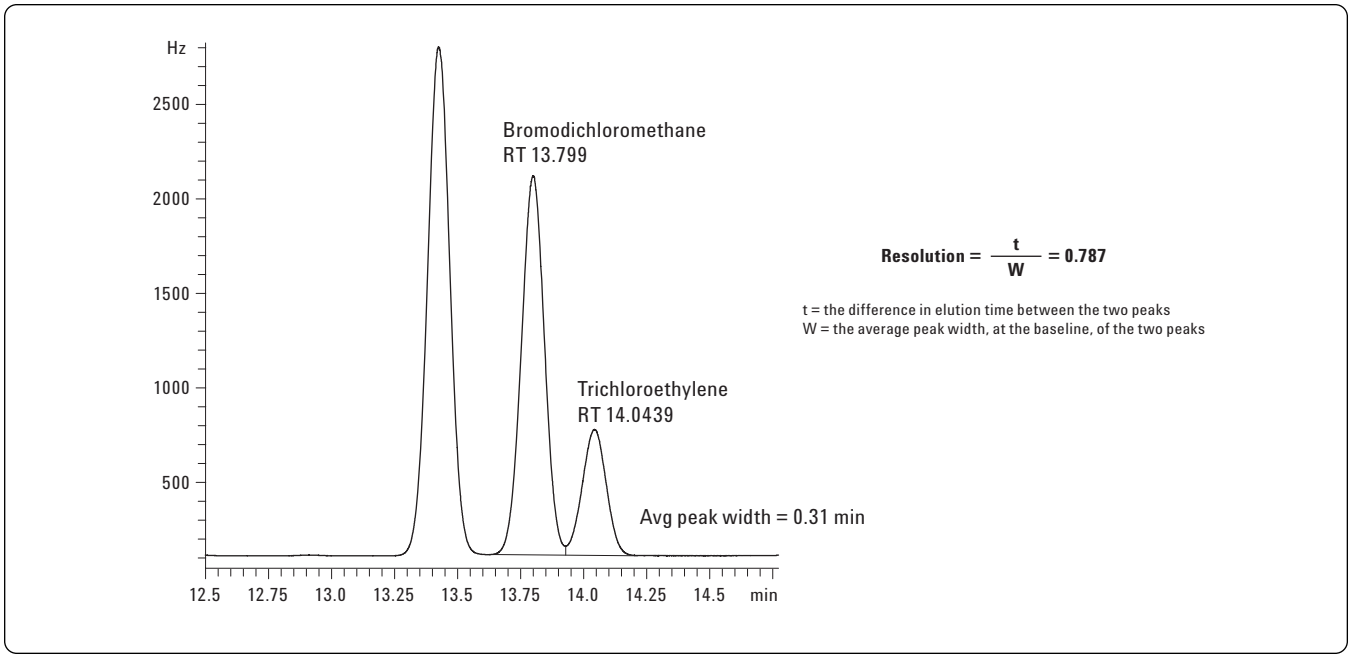


Figure 6. Enlarged chromatogram of 0.05 µg/mL EPA 551.1 standard on the Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm capillary GC column. Method criteria for column performance is a resolution greater than 0.50 between bromodichloromethane and trichloroethylene.

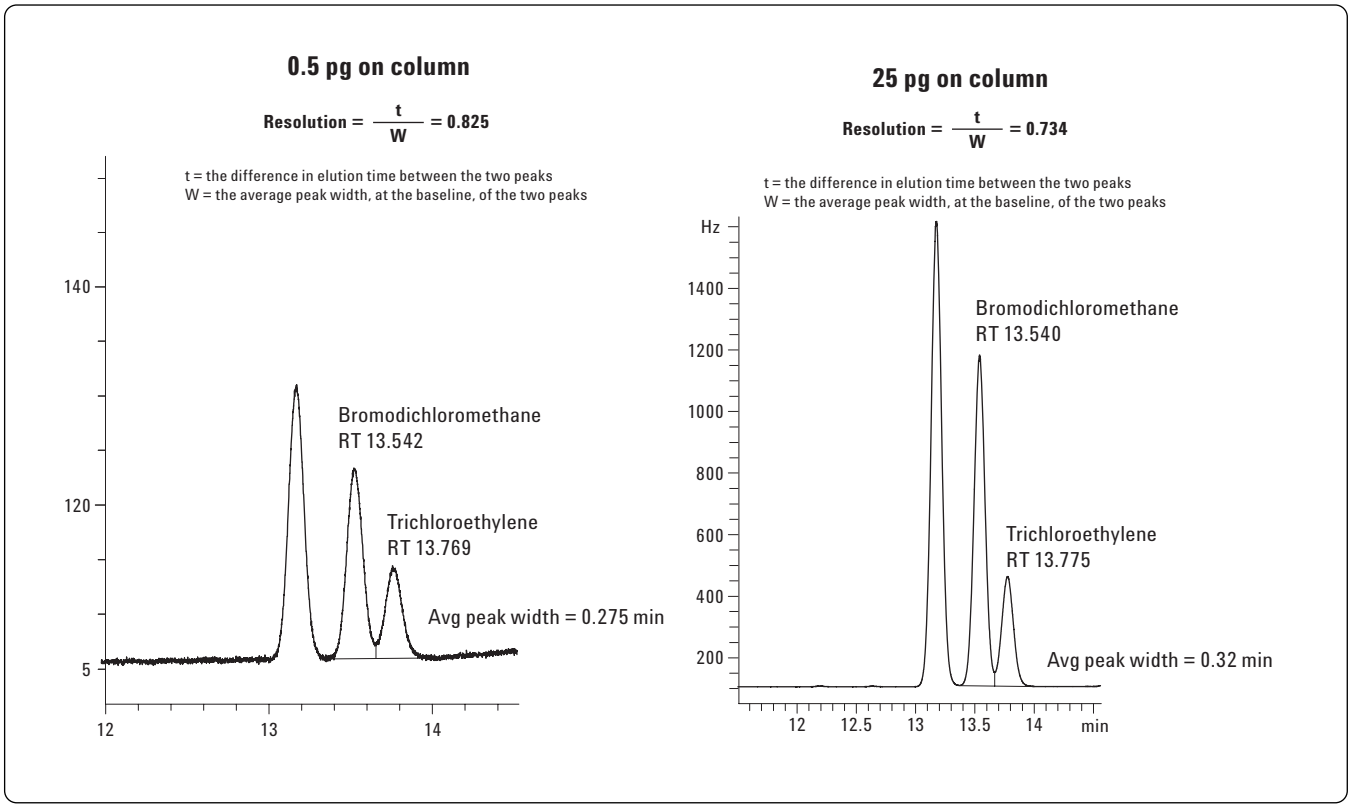


Figure 7. Enlarged chromatograms of the low and high range EPA551.1 standards on the Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm × 1.0 µm capillary GC column. Method criteria for column performance is a resolution greater than 0.50 between bromodichloromethane and trichloroethylene.

Table 4. Peak Identification Table for EPA551.1 Chromatograms Shown in Figures 2 Through 4

Peak number	Peak name
1	Chloroform
2	1,1,1-Trichloroethane
3	Carbon tetrachloride
4	Trichloroacetonitrile
5	Dichloroacetonitrile
6	Bromodichloromethane
7	Trichloroethylene
8	Chloral hydrate
9	1,1-Dichloro-2-propanone
10	1,1,2-Trichloroethane
11	Chloropicrin
12	Dibromochloromethane
13	Bromochloroacetonitrile
14	1,2-Dibromoethane
15	Tetrachloroethlyene
16	1,1,1-Trichloro-2-propanone
17	Bromoform
18	Dibromoacetonitrile
19	1,2,3-Trichloropropane
20	1,2-Dibromo-3-chloropropane

Conclusions

This application successfully demonstrates the use of an Agilent J&W HP-1ms Ultra Inert capillary GC column for primary analysis of EPA 551.1 chlorinated solvents, trihalomethanes, and disinfection by-products. Linearity was excellent for all organochlorine analytes studied, yielding 0.998 or greater R^2 values down to a 0.5 pg on-column loading. One of the reasons for the excellent linearity and high R^2 values is the highly inert surface of the column. The excellent peak shape of the chloral hydrate and resolution between bromodichloromethane and trichloroethylene emphasize the advantage of the Agilent J&W HP-1ms Ultra Inert capillary GC column. The lack of chemically active sites makes this column an excellent choice for EPA Method 551.1 analysis.

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