Application Note

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Fast Analysis of 18 Polychlorinated Biphenyls (PCBs) Using the Agilent Intuvo 9000 GC Dual ECD

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Abstract

This application note describes polychlorinated biphenyl (PCB) analysis based on electron capture detector (ECD) detection and dual-column confirmation approach on the Agilent Intuvo 9000 GC. The Agilent Method Translator tool easily and effectively translated an original China HJ method based on 320 µm columns and N_2 as carrier gas to a fast method based on 180 µm columns and H_2 as carrier gas. A fast analysis, completed in approximately six minutes, was achieved on 180 µm high-efficiency columns under the optimized fast oven ramp rate. In addition, a fast PCB analysis was also realized on 250 µm columns within 10 minutes. The Agilent Intuvo inlet splitter chip simplified the setup of the analytical system by delivering an easy and reliable connection of dual columns with a single common inlet and dual ECDs.

Introduction

PCBs were once extensively used in industrial applications as coolants and lubricants, and persist in the environment. Their production in China started in 1965 and ceased at the end of 1974. During these 10 years, 10,000 tons of PCBs were produced. They entered air, water, and soil during its manufacturing, storage, disposal, and industrial applications. Due to their environmental persistence, PCBs continue to cycle on Earth, even though production was banned 40 years ago.

The PCB family has 209 congeners, defined by the position of chlorines on the biphenyl molecules. Gas chromatography (GC) is often used to measure PCB contamination in the environment. The electronegative chlorines on the PCB biphenyl rings show good response in ECD, and so GC-ECD is a key technique for PCB analysis. To date, it has not been possible to separate all PCBs on a single column. In addition, the sample matrix can interfere with PCB identification. Even if the ECD is a selective detector, it is possible to generate false positive qualification results based on the retention times (RT) generated on one analytical column. To reduce the possibility of false positive identification, analysts deploy a dual-column confirmation approach by separating PCBs on two columns with different selectivity. The chance of two or more congeners coeluting on two columns with different stationary phase is much less than on one column, thus the identification accuracy is greatly improved.

HJ 922-2017 is a standard published by the Ministry of Ecology and Environment of the People's Republic of China. This standard guides the measurement of 18 critical PCBs in soil and sediments using a GC-ECD technique.[1] Dual-column confirmation is recommended in this standard. The general analysis time achieved with the air-bath oven, as shown in the HJ 922-2017 standard, is approximately 25 minutes. In this application note, fast PCB analysis based on Agilent high-efficiency columns and the Intuvo direct heating oven was performed within six minutes. The repeatability and linearity of the fast-analysis method were evaluated by PCB calibration standards according to the HJ922-2017 method. Besides the fast method developed on 180 µm high-efficiency columns, we considered that some environmental or contract labs are usually equipped with 250 µm columns for routine analysis. A fast method based on 30 m × 250 µm capillary columns was also developed for 18 PCBs analysis with H_2 as carrier gas.

Experimental

PCB calibration standards were analyzed on an Agilent Intuvo 9000 GC/ECD system. The 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 split ratio was approximately 1:1 because the two analytical columns have similar dimensions/restrictions, which help generate an equal split between two columns.

Table 1. Analytical parameters and consumables used on the Agilent Intuvo 9000 GC/dual ECDs system.

Agilent Intuvo 9000 GC/ECD Instrument Parameters			
Fast Method Number		Method No. 1 for 180 µm Intuvo column	Method No. 2 for 250 µm Intuvo column
Autosampler		Agilent 7650A automatic liquid sampler	
Split/Splitless Inlet Mode		Splitless	Splitless
Inlet Temperature		260 °C	260 °C
Purge Flow		60 mL/min	60 mL/min
Purge Time		0.75 min	0.75 min
Intuvo Flow Path	Guard Chip	260 °C	260 °C
	Bus	280 °C	280 °C
Carrier Gas		Hydrogen	Hydrogen
Column Flow Rate		2.25 mL/min, constant flow	3.12 mL/min, constant flow
Oven Ramp Program		100 °C, hold 0 min 72.326 °C/min to 220 °C, hold 1.04 min 72.326 °C/min to 260 °C, hold 4.15 min	100 °C, hold 0 min 42.571 °C/min to 220 °C, hold 1.77 min 42.571 °C/min to 260 °C, hold 7.07 min
ECD Temperature		280 °C	
ECD Make Up Flow		60 mL/min, N_2 Column + makeup = constant	
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, 20 m × 0.18 mm, 0.18 µm (p/n 121-5522-UI-INT) **Column 2:** J&W DB-1701, 20 m × 0.18 mm, 0.18 µm (p/n 100-2111-INT, custom Intuvo column)	**Column 1:** Agilent J&W DB-5ms UI, 30 m × 0.25 mm, 0.25 µm (p/n 122-5522-UI-INT) **Column 2:** J&W DB-1701 Intuvo, 30 m × 0.25 mm, 0.25 µm (p/n 122-0732-INT)

The system analytical parameters are shown in Table 1 for 180 and 250 µm columns. The GC oven program and column flow rate parameters used in the HJ922-2017 standard are shown in the Agilent *Method Translator* tool interface (Figure 3).

Chemicals and standards

The PCB stock solution: 100 mg/L PCB mixture in hexane was purchased from ANPEL Laboratory Technologies (Shanghai) Inc. The PCBs working solutions were prepared by diluting the stock solutions to 1 mg/L.

Seven calibration levels are prepared by adding aliquots of working solution to 10 mL of hexane. The targeted concentrations were approximately 5, 10, 20, 50, 100, 200, and 500 µg/L.

Results and discussion

Following the analytical conditions in the HJ922-2017 standard,[1] the chromatograms of 50 µg/L PCBs on 30 m × 320 µm, 0.25 µm DB-1701 and DB-5ms columns are shown in Figures 1A and 1B. With the column flow rate set at 2 mL/min as recommended by HJ922-2017, the resolution of three critical PCB pairs (i.e., PCB123/PCB118, PCB153/PCB105, PCB156/PCB157) on the DB-5ms column was not good. This poor resolution is probably caused by the applied high linear velocity of N_2 at 2 mL/min. If the N_2 flow rate was reduced to 1 mL/min, the resolution of PCB123/118, PCB 153/105, and PCB156/157 was improved from 0.88 to 1.11, 0.84 to 1.31, and 1.11 to 1.38, respectively. However, the analysis time

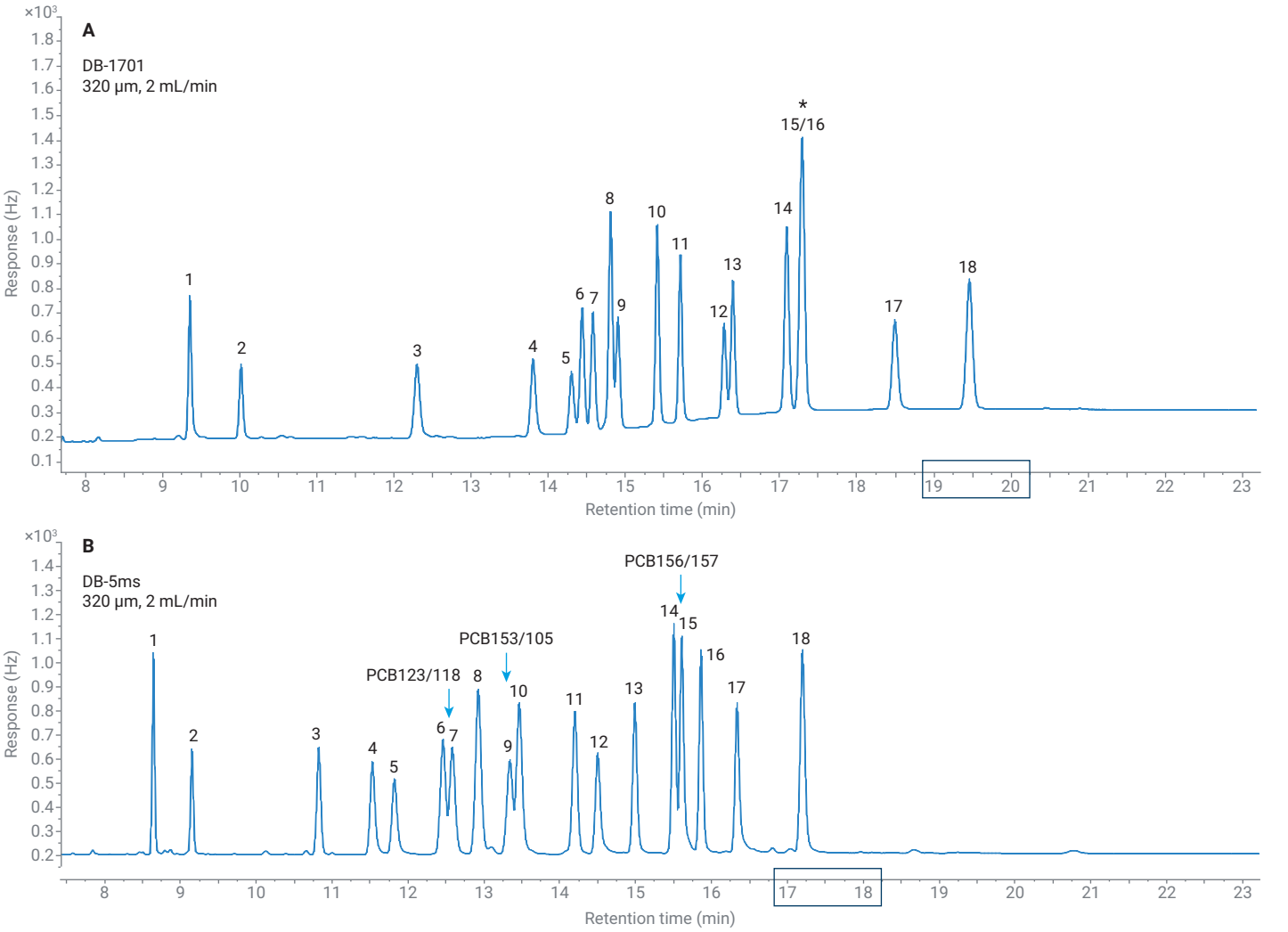

Figure 1. PCBs analysis on 30 m × 320 µm × 0.25 µm DB-1701 (A) and DB-5ms (B) columns with 2 mL/min carrier gas (N_2). (*PCB157 and PCB180 coeluted on the DB-1701 column, which is caused by the limited selectivity of DB-1701 towards the two components. The coelution is consistent with the reference chromatogram in the HJ922-2017 standard).

was increased by approximately 20%, as shown in Figures 2A and 2B (the analysis time was defined as the retention time of the last eluted compound, PCB189). To reduce the analysis time without compromising the resolution, 180 µm high-efficiency columns and H_2 as carrier gas were used for fast PCB analysis on the Intuvo 9000 GC/ECD system.

With the assistance of Method Translator, the original analytical parameters based on a 30 m × 320 µm, 0.25 µm column and 1 mL/min carrier gas flow rate (N_2) were translated into a new set of parameters based on a 180 µm column with H_2 carrier gas, as shown in Figure 3. Method Translator is a tool embedded in Agilent chromatography data systems (CDS), including Agilent OpenLab CDS, to facilitate new method development based on an existing method. The chromatograms achieved using the new method are shown in Figure 4. The 18 compounds can be well separated on the 20 m × 180 µm DB-5ms and DB-1701 columns. The resolution of PCB123/PCB118, PCB153/PCB105, and PCB156/PCB157 on Intuvo DB-5ms are 1.14, 1.39, and 1.47,

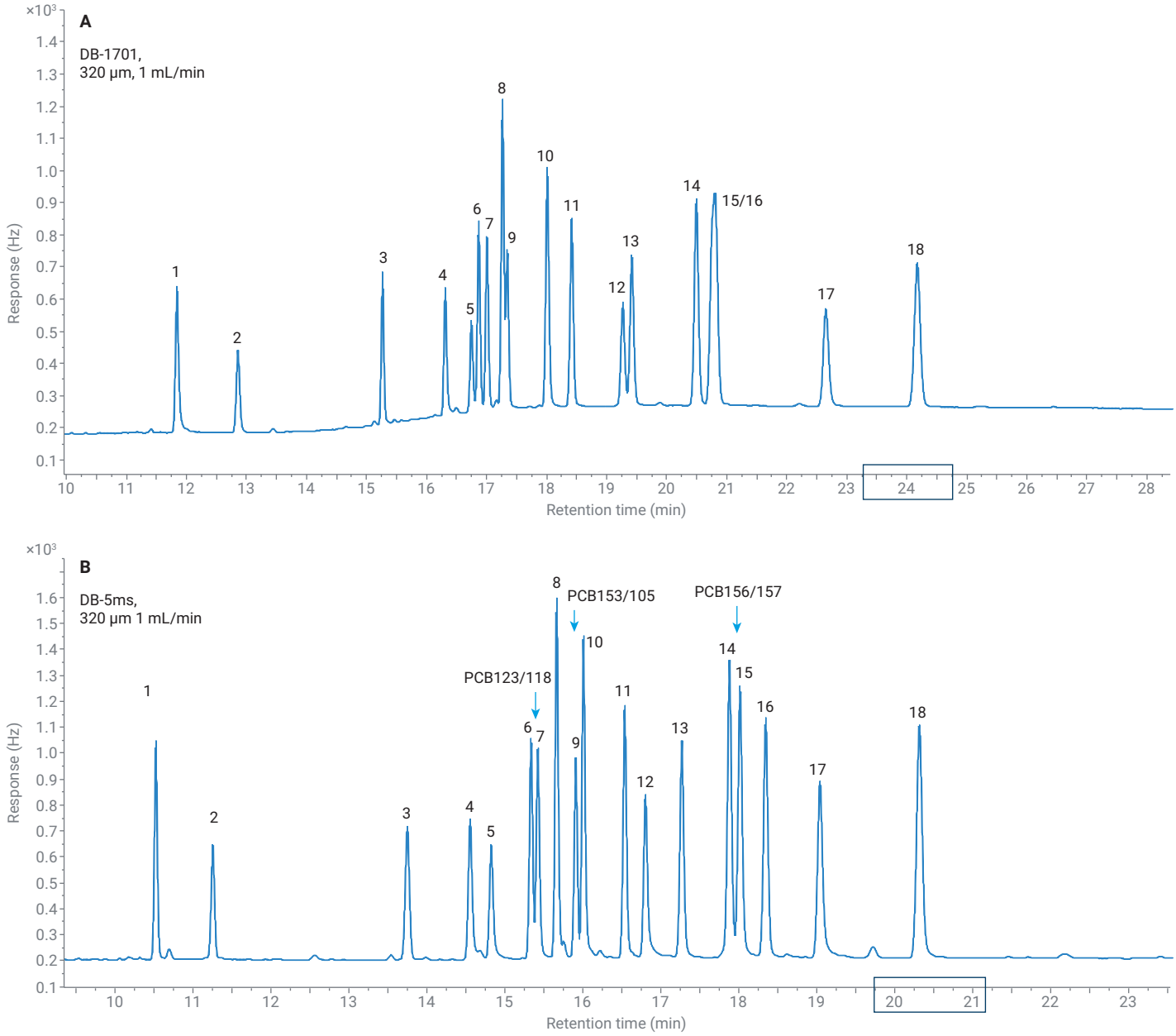

Figure 2. PCBs analysis on 30 m × 320 µm, 0.25 µm DB-1701 (A) and DB-5ms (B) columns with 1 mL/min carrier gas (N_2).

better than those obtained on 320 µm columns. The resolution improvement is understandable because the phase ratio of the newly used columns is lower than that of 320 µm × 0.25 µm column, coupled with the thinner column internal diameter, which helps generate better resolution on 180 µm × 0.18 µm columns. The analysis was finished within six minutes, a roughly 70% speed gain achieved compared to the analysis on 320 µm columns.

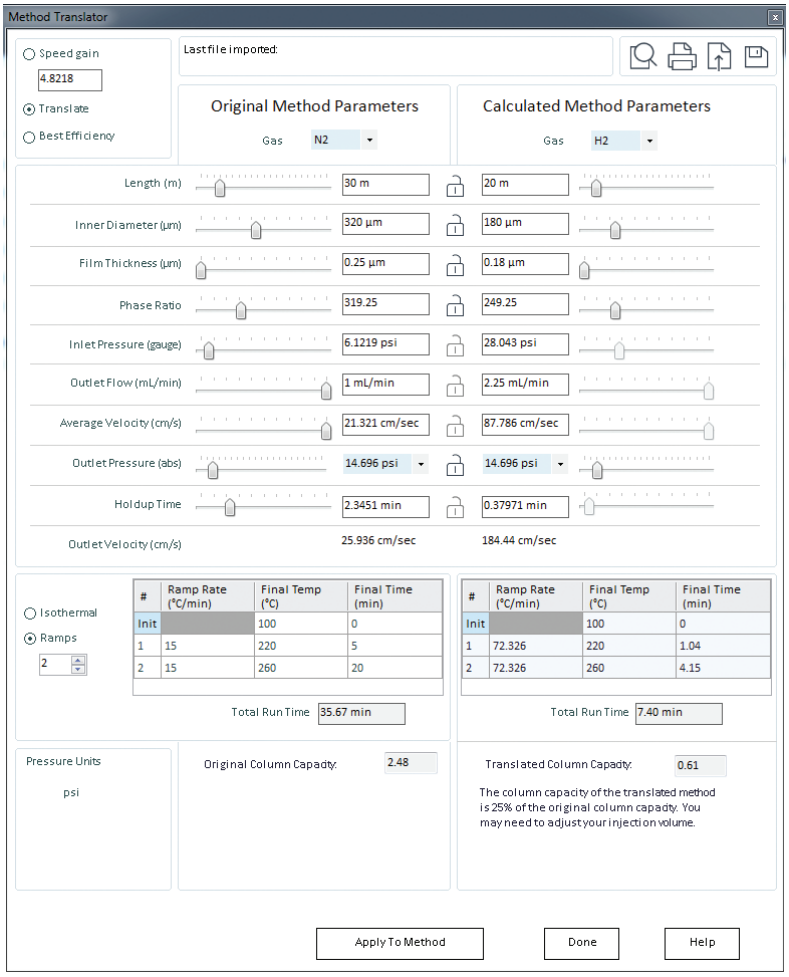

Figure 3. Translation of the original HJ922-2017 method to a fast method on the Agilent Intuvo 9000 GC using Agilent Method Translator.

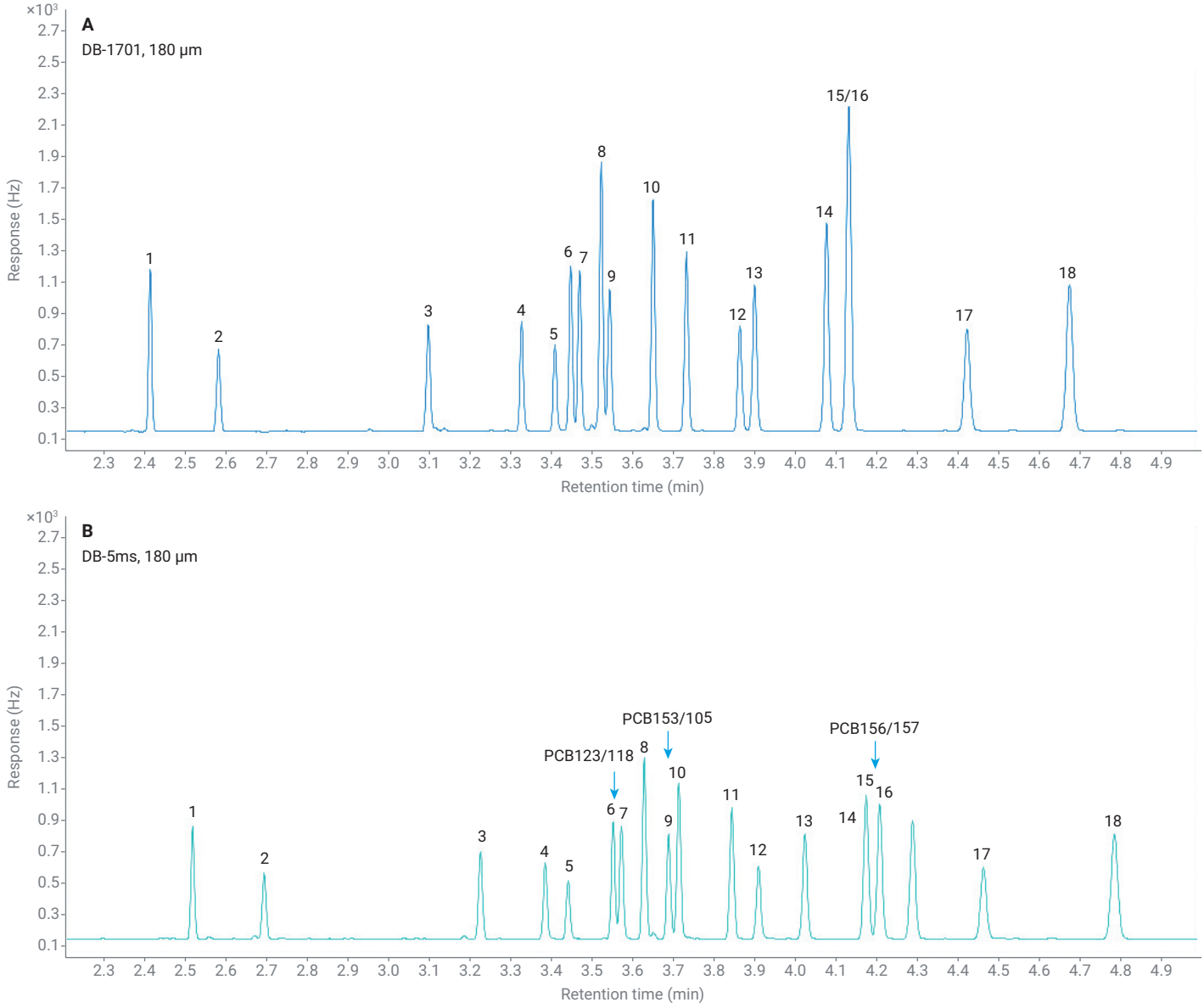

Figure 4. PCBs analysis on 20 m × 180 µm, 0.18 µm DB-1701 (A) and DB-5ms (B) columns with 2.25 mL/min carrier gas (H_2).

The retention times (RT) of 18 PCBs on the primary qualification/quantitation column (DB-5ms) and the confirmation column (DB-1701) are tabulated in Table 2. The RT and area repeatability of the fast analysis was evaluated by seven consecutive runs of 20 µg/L calibrant. RT RSD% on DB-5ms is from 0.01 to 0.024%, and 0.007 to 0.010% on DB-1701 (Figure 5). Area RSD% on ECD2 (connected to DB-5ms) ranged from 0.8 to 1.4% and 0.7 to 1.5% on ECD1 (connected to DB-1701), as shown in Figure 6. The overlaid chromatograms of seven injections on the DB-5ms column are shown in Figure 7. The excellent repeatability proved that the Intuvo 9000 GC can provide highly precise thermal and pneumatic control under a fast oven ramping rate.

The ECD linearity on calibration range of 5 to 500 µg/L was evaluated at seven concentration levels. In real analysis, the calibration formulas developed with the DB-5ms column were used for quantitation. The regression formulas of 18 calibration curves on the DB-5ms column are listed in Table 2. The linearity correlation coefficients are in the range of 0.9990 to 0.9998, better than the requirement of 0.995 specified in the HJ922-2017 standard.

The instrument detection limits of 18 PCBs with a signal-to-noise ratio (SNR) of 3:1 were calculated based on the chromatogram of a 2 µg/L standard. The calculated detection limits are shown in Table 2, which can be used as a reference to understand the detectability of the targeted PCBs by the Intuvo 9000 GC/ECD system.

Table 2. PCBs RT, linear calibration formulas, correlation coefficients, and calculated IDL based on SNR on the 180 µm Agilent J&W DB-5ms Intuvo column.

Peak Number	PCB Congener Number	RT /min		Regression Formula on DB-5ms Column	Square of Regression Coefficient (R^2)	IDL (µg/L)
		DB-5ms	DB-1701			
1	PCB28	2.519	2.415	y = 13.6605x + 0.9986	0.9990	0.094
2	PCB52	2.695	2.582	y = 7.6590x + 43.1920	0.9997	0.084
3	PCB101	3.227	3.098	y = 10.9344x + 36.7416	0.9998	0.088
4	PCB81	3.386	3.328	y = 9.6660x + 18.7313	0.9997	0.106
5	PCB77	3.442	3.409	y = 7.1742x + 23.4441	0.9997	0.056
6	PCB123	3.553	3.448	y = 15.4786x + 3.7303	0.9996	0.057
7	PCB118	3.573	3.47	y = 14.8620x + 7.6712	0.9997	0.039
8	PCB114	3.629	3.523	y = 26.4850x – 59.0785	0.9993	0.060
9	PCB153	3.689	3.544	y = 13.5290x + 29.5189	0.9998	0.041
10	PCB105	3.714	3.651	y = 23.8360x – 49.301	0.9993	0.048
11	PCB138	3.845	3.733	y = 19.3741x + 5.2154	0.9997	0.073
12	PCB126	3.91	3.864	y = 11.0658x + 15.2021	0.9996	0.055
13	PCB167	4.024	3.9	y = 16.8274x + 5.2525	0.9996	0.042
14	PCB156	4.175	4.077	y = 26.8929x – 56.8413	0.9992	0.044
15	PCB157	4.208	4.132	y = 25.3124x – 38.0390	0.9994	0.053
16	PCB180	4.289	4.132	y = 22.0947x – 3.7871	0.9997	0.069
17	PCB169	4.463	4.423	y = 14.1688x + 15.9701	0.9995	0.054
18	PCB189	4.786	4.675	y = 25.8732x – 24.2229	0.9997	0.053

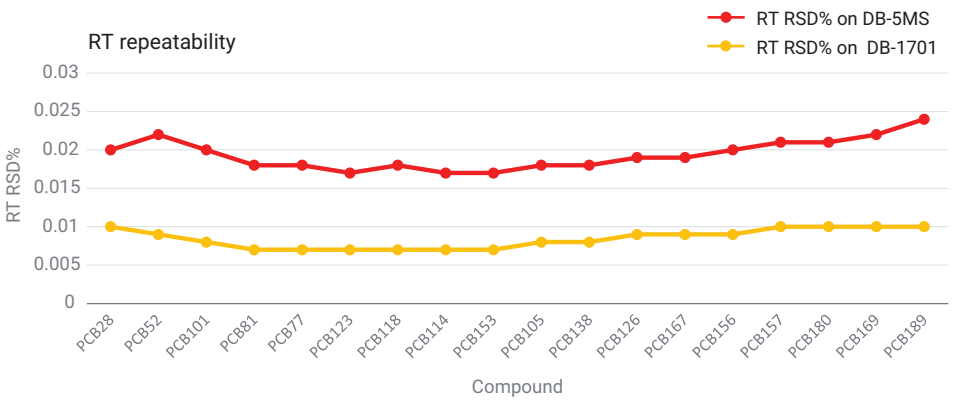

Figure 5. RT repeatability of 18 PCBs on Agilent Intuvo DB-5ms and DB-1701 columns.

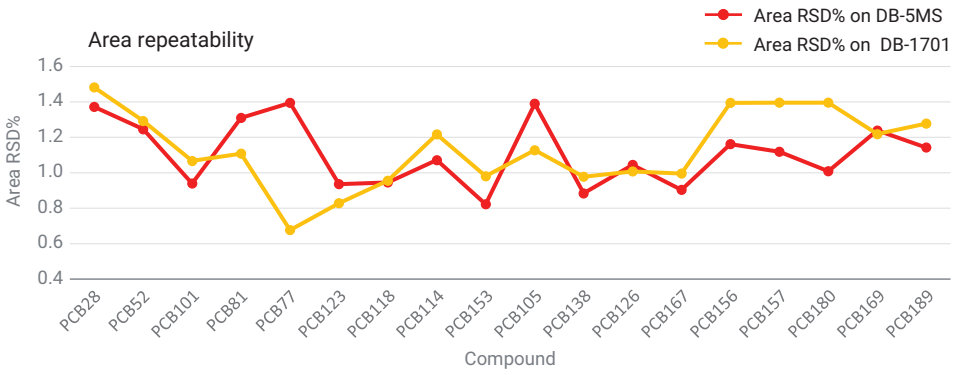

Figure 6. Area repeatability of 18 PCBs on ECD1 connected to a 180 µm Intuvo DB-1701 column and ECD2 connected to a 180 µm Intuvo DB-5ms column.

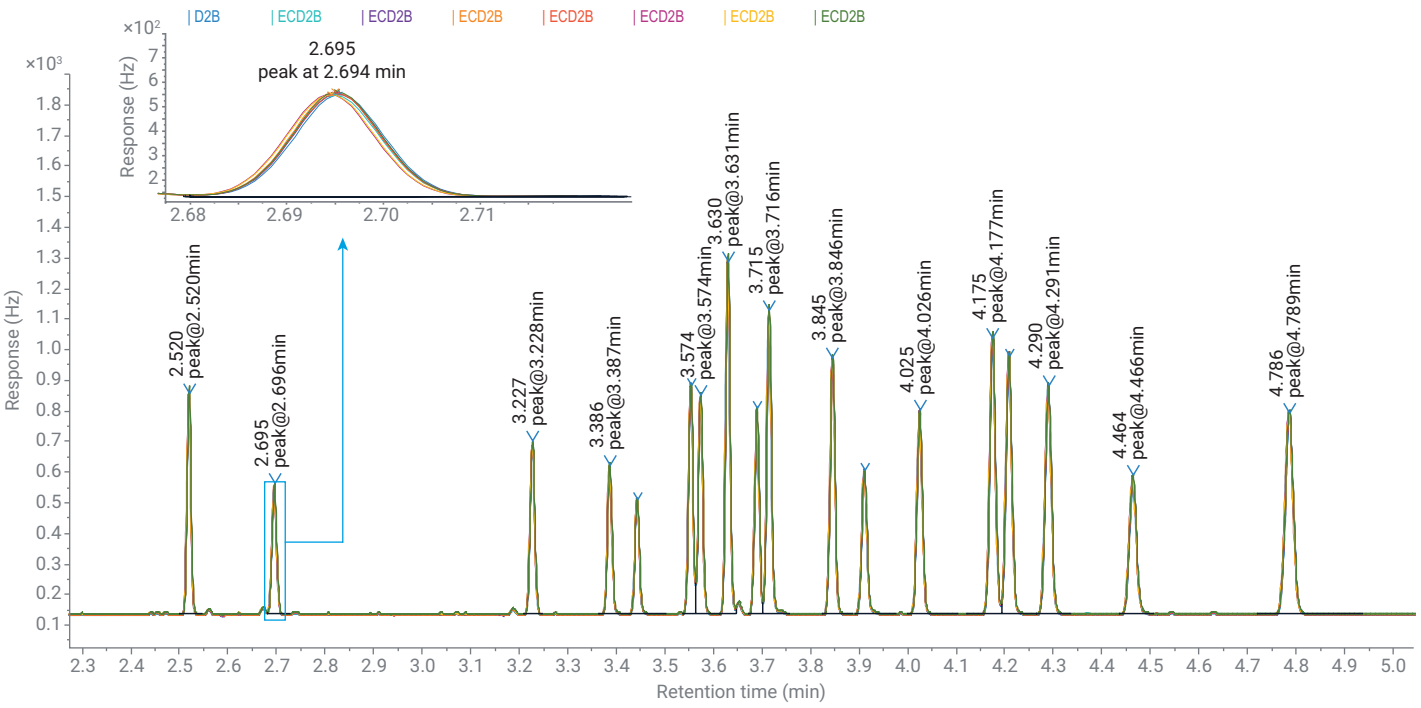

Figure 7. Overlaid chromatograms of 20 µg/L calibrants on Agilent J&W DB-5ms column.

A real soil sample was prepared according to the HJ922-2017 sample preparation procedure. The extracts were purified and concentrated in hexane for analysis. The chromatograms of the real sample were overlaid with the chromatograms of the calibrant (Figure 8). No PCBs were identified based on the combined qualification results on the two columns. Some components were "identified" on the primary column, but couldn't be detected on the confirmation column.

Compared to 180 µm id columns, 250 µm id columns are more common in routine analytical labs. The PCB analysis on a 250 µm column with H_2 as carrier gas is not as fast as that performed on a 180 µm high-efficiency column. However, its speed can surpass that generated on a 320 µm column with N_2 as carrier gas. In this application note, fast separation method no. 2 was based on 250 µm DB-5ms and DB-1701 Intuvo columns and was also developed with the Method Translator tool. The PCB calibration standard was analyzed using this translated method (the corresponding GC parameters can be referred to in Table 1). Representative chromatograms are shown in Figure 9. PCB 189, the last analyte, eluted at approximately 9 minutes off the DB-1701 column. The RT is twice as long as that on the 180 µm column but only half of that on the 320 µm column with N_2 as carrier gas. Meanwhile, it was observed the resolution of PCB123/PCB118, PCB153/PCB105, and PCB156/PCB157 on the Intuvo 30 m × 250 µm columns are quite good. The RT and area repeatability on 30 m × 250 µm columns were evaluated by 10 consecutive injections of 20 µg/L calibrant. The RT RSD% on the DB-5ms column ranged from 0.013 to 0.02% and area RSD% from 0.814 to 1.735%. The RT RSD% on the DB-1701 column is from 0.006 to 0.01% and area RSD% from 1.094 to 1.927%. The test results demonstrated that the Intuvo 9000 GC configured with 250 µm columns can also be used to accelerate the PCB analysis, with excellent chemical performance. Environmental or contract labs can choose the fast PCBs analysis method, either based on 180 or 250 µm columns, according to their own analysis speed requirements and column availability in the labs.

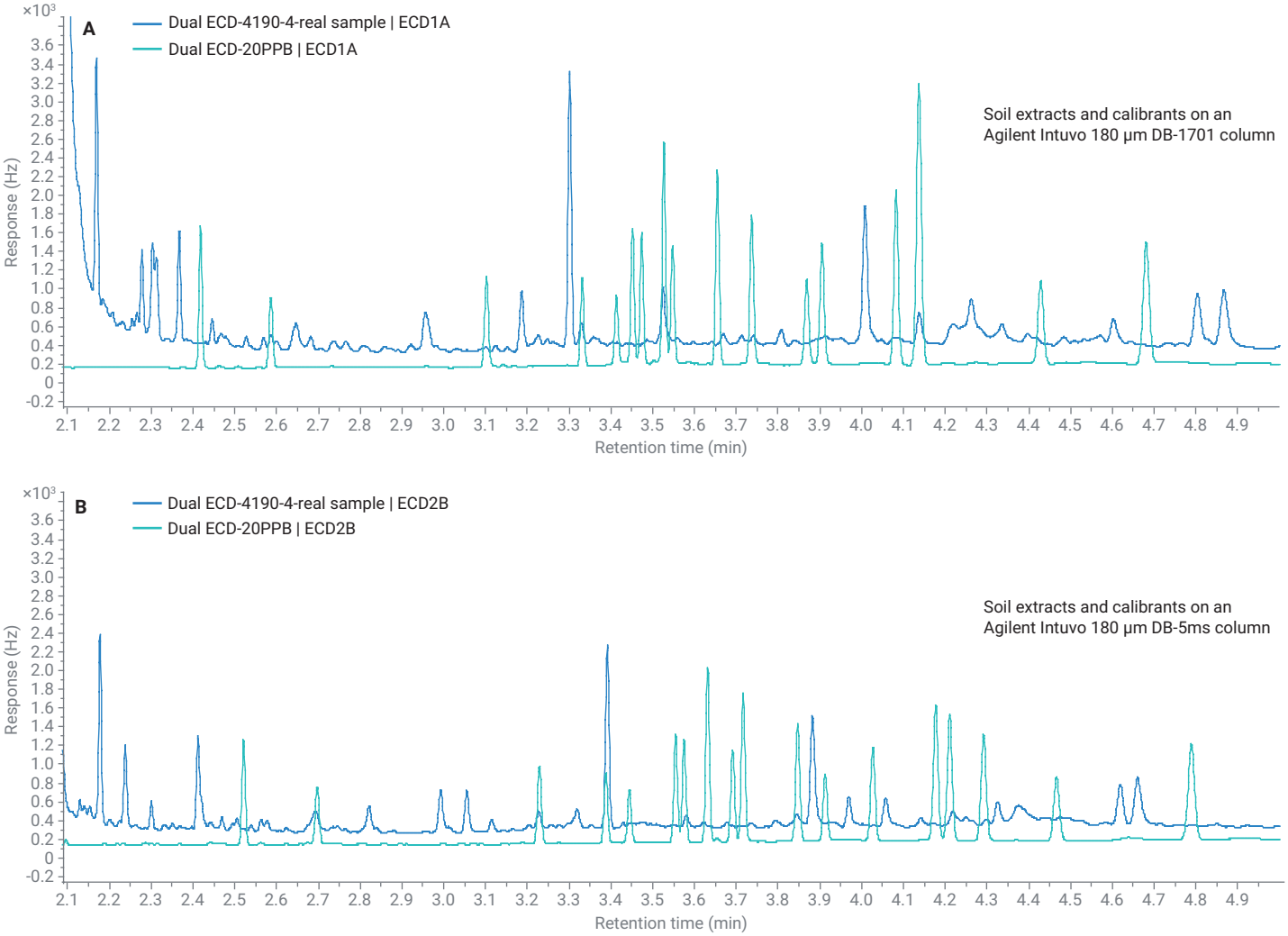

Figure 8. Soil extracts analysis on Agilent Intuvo 9000 GC configured with 180 µm DB-5ms and DB-1701 columns.

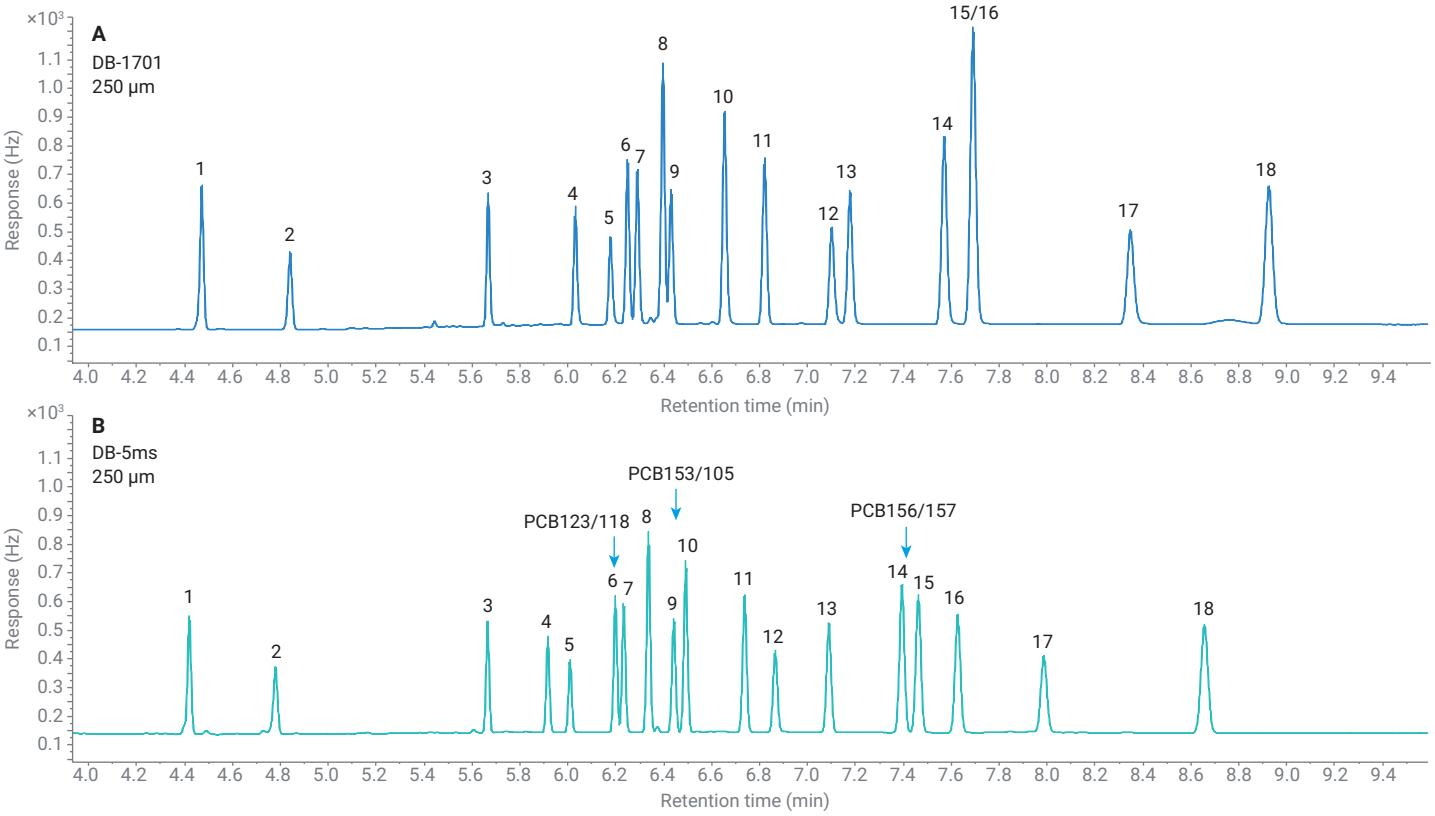

Figure 9. PCB analysis on 30 m × 250 µm, 0.25 µm DB-1701 (A) and DB-5ms (B) columns with 3.13 mL/min carrier gas (H_2).

Conclusion

A fast method was developed on an Intuvo 9000 GC/ECD system for 18 indicator PCBs analysis by referring to China HJ922-2017 standard. Two 20 m × 180 µm columns were deployed for their high efficiency. Hydrogen was used as carrier gas because it can generate low HETP at quite high linear velocity. Method Translator helped translate the original HJ922-2017 method to the new fast method. This translation tool was easy to use and saved time spent on method development. The separation based on the fast method gave equivalent or better resolution compared to the original method.

The analysis time was decreased from 25 to 6 minutes with excellent RT and area repeatability. The method linearity was evaluated from 5 to 500 µg/L. The correlation coefficients of the linear calibration curve are better than 0.995, exceeding HJ922-2017 requirement. For an analytical lab equipped with 30 m × 250 µm Intuvo DB-5 and DB-1701 columns, the 18 PCBs can be analyzed within nine minutes by applying the other translated method on 250 µm columns with H_2 as carrier gas. The above test results demonstrate the Intuvo 9000 GC/ECD platform can provide fast and reliable analysis of 18 indicator PCBs as required by the China HJ922-2017 standard.

Reference

1. Soil and Sediment–Determination of Polychlorinated Biphenyls–Gas Chromatography, HJ 922-2017, Ministry of Ecology and Environment of the People's Republic of China.

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