Application Note

Environmental

Analysis of Polychlorinated Biphenyls on the Agilent 8890 GC/5977B GC/MSD by Following the China HJ 743-2015 Method

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Abstract

This Application Note describes using the Agilent 8890 GC/5977B GC/MSD to analyze 18 polychlorinated biphenyls (PCBs) following the HJ 743-2015 method. The instrument repeatability, linearity, and detection limit (LOD) were investigated according to PCB calibration standards. The method recovery rate was assessed on spiked quartz sand and soil sample.

Introduction

For many years, PCBs were widely used as dielectrics and in electrical apparatus coolant fluid, but when they were identified as environmentally toxic, PCBs were classified as persistent organic pollutants. As a result of broad usage and environmental persistence, PCBs still exist in the environment, especially in water sources and soils.

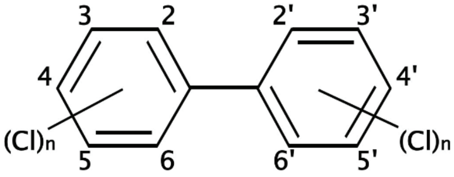


Figure 1. The general chemical structure of polychlorinated biphenyl (PCB).

In China, the production of PCBs began in 1965 and ceased at the end of 1974. Internationally, United States federal law banned the production of PCBs in 1978, and PCB production was banned at the Stockholm Convention on Persistent Organic Pollutants in 2001. Over the years of 1965 to 1974, PCB production amounts in China reached 10,000 tons. Of this amount, appproximately 9,050 tons of tri-PCBs were used for transformers and appproximately 1,000 tons of penta-PCBs were used as additives in paints. When PCB production ceased, the 750,000 transformers containing PCBs were discarded from 1980 to 1990. Currently, most of the transformers are being emptied into containers and sealed in caves or in cellars. However, due to factors such as long-term storage, rotting of storage containers materials, and other similar damages, leakages have occurred. This was confirmed by high PCB content found in soil surrounding dumping sites.

There are 209 congeners in the PCB family. To evaluate all congeners on one column is the ultimate goal of PCB analysis and although progress has been made, this has not been achieved yet. In China, there are several national standards that guide the analysis of PCBs in different matrices, such as HJ 743-2015,[1] HJ 715-2014,[2] and HJ 891-2017.[3] These HJ methods were developed, verified, and published by the Ministry of Ecology and Environment of the People's Republic of China, and were used to guide the measurement of 18 critical PCBs in the environment. Among the 18 targeted PCB congeners, six congeners are indicator PCBs, and 12 are coplanar PCBs. Coplanar PCBs are dioxin-like PCBs with high environmental toxicity.

GC electron capture detector (ECD) and GC mass selective detector (MSD) are the techniques generally applied to PCB analysis. For GC detector-based method,[4] dual columns, each coated with either apolar or polar stationary phase, are used for PCB separation and identity confirmation. The ECD generates a high response on the electronegative chlorine in PCB structure for sensitive and selective detection. For the GC/MSD-based method, retention time (RT) and characteristic ions of each PCB can be used for congener identification. The selective monitoring of MSD on targeted ions ensures fewer false positive identifications compared to the GC-ECD analysis approach, especially under the interference of heavy matrix.

In this Application Note, the Agilent 8890 GC/5977B GC/MSD platform was used for the analysis of 18 PCBs by following HJ 743-2015 standard. The platform performance was evaluated in terms of linearity, repeatability, and instrument detection limit for the 18 targeted PCBs.

Experimental

The PCB analysis was performed using an Agilent 8890 GC/5977B GC/MSD system equipped with an Agilent DB-5ms column. Sample introduction was done using the Agilent 7695A 50-vial automatic liquid sampler with a 10 µL syringe and a split/splitless injection port. Table 1 shows the instrument conditions. Table 2 lists the consumables used in the experiment.

Agilent MassHunter Acquisition software version 10.0 was used for data collection. MassHunter Qualitative Analysis version B.07.00 and MassHunter Quantitative Analysis version B.08.00 were used for data analysis.

Chemicals and standards

The stock solution:
100 mg/L PCBs mixture in hexane, 1,000 mg/L tetrachloro-*m*-xylene (TCMX) in hexane and 100 mg/L 2,2',4,4'5,5'-hexabromobiphenyl (PBB-153) in hexane were purchased from ANPEL scientific instrument. TCMX was used as surrogate, and PBB-153 was the internal calibration standard. The working solutions for PCBs calibrant, surrogate, and ISTD were made by diluting the stock solutions to 1, 5, and 10 mg/L with hexane. Decafluorotriphenylphosphine (DFTPP) in dichloromethane was purchased from ANPEL. It was diluted to 2.5 mg/L in hexane for mass spectrometer performance verification.

Six calibration levels were made by adding aliquots of working solution in 10 mL hexane. The targeted concentrations were approximately 10, 20, 50, 100, 200, and 500 µg/L. The concentration of internal standard was 800 µg/L so it can generate a similar response compared to those produced by PCB calibrants at middle level calibration concentration.

The PCB extracts from the soil sample was provided by the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences. The sample preparation followed the procedure described in HJ 743-2015.

Results and discussion

HJ 743-2015 recommends a 5% phenyl 95% dimethylpolysiloxane-type stationary phase for the 18 PCB analysis. The Agilent HP-5ms column is coated with this type of polymer. Meanwhile, the Agilent DB-5ms column is coated with 5% phenyl 95% dimethyl arylene siloxane, and has similar selectivity as the HP-5ms column. Both HP-5ms and DB-5ms columns were tested for their resolution of the targeted analytes. The chromatograms of the 18 PCBs calibration standard on DB-5ms column showed better resolution on PCB123 and PCB118 (Figure 2). The DB-5ms column was used for the following tests.

Table 1. Instrument configuration and analytical parameters.

Agilent 8890 GC/5977B GC/MSD instrument parameters	
Autosampler	Agilent 7650A automatic liquid sampler
Split/Splitless Inlet Mode	Splitless
Inlet Temperature	280 °C
Purge Flow	60 mL/min
Purge Time	0.75 min
Carrier Gas	Helium
Column Flow Rate	1.2 mL/min, constant flow
Oven Ramp Program	40 °C, hold 0 minutes 20 °C/min to 230 °C, hold 0 minutes 5 °C/min to 260 °C, hold 1.5 minutes 20 °C/min to 310 °C, hold 2 minutes
Transfer Line Temperature	300 °C
Extraction Ion Source Temperature	250 °C
MS Quad Temperature	150 °C
Acquisition Type	SIM
EMV Mode	Gain factor
Gain Factor	0.5

Table 2. Consumables used for the application development.

Consumable types	Description and part number
Syringe	Agilent ALS syringe, 10 µL tapered, fixed needle (p/n 5181-3354)
Vials	Agilent A-line certificated 2 mL amber screw top vials (p/n 5182-0716)
Vials Screw Cap	Agilent screw cap, blue, certified, PTFE/silicone/PTFE septa (p/n 5182-0723)
Column	Agilent DB-5ms, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532)
Liner	Agilent Ultra Inert, splitless liner with glass wool (p/n 5190-2293)
Septum	Agilent bleed temperature optimized, nonstick 11 mm septa (p/n 5183-4757)

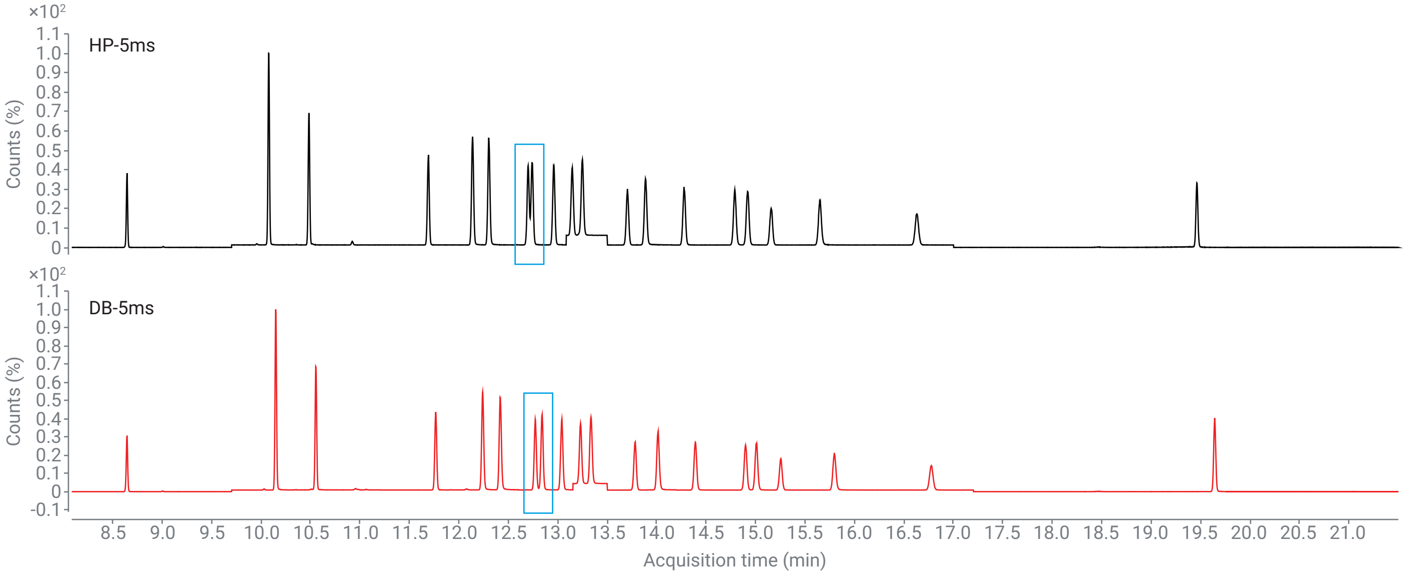


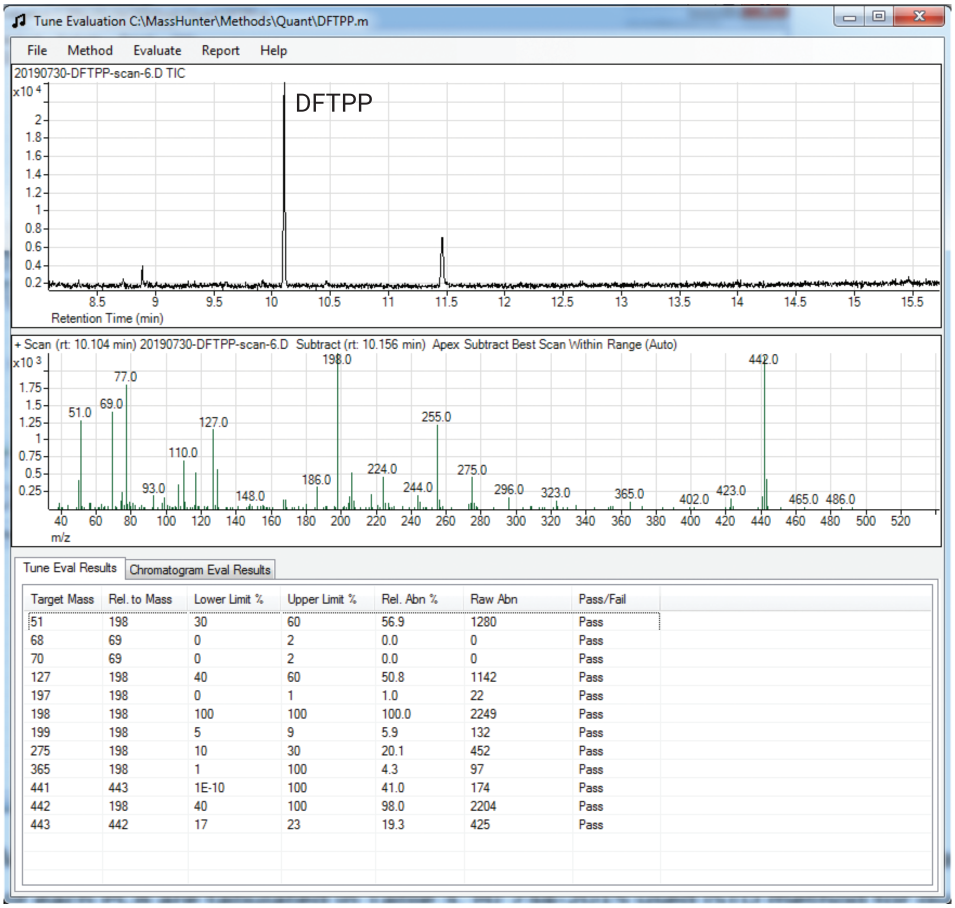
Figure 2. Chromatograms of 18 PCBs analyzed on Agilent HP-5ms and DB-5ms columns.

According to HJ 743-2015, the MSD should be checked daily to ensure data validity and reliability. The MSD was autonomously tuned in DFTPP tune mode. The tune result was evaluated by injection of 1 µL of 2.5 mg/L DFTPP in hexane. Figure 3 shows the conformity of the tune result to the requirement of HJ 743-2015 on MSD performance.

The MSD data for PCB standards were acquired in SIM mode. The quantifier ion and qualifier ions of each PCB are tabulated in Table 3.

Seven injections of calibration standards at 10 and 50 µg/L respectively were run for instrument repeatability assessment. The response factor (RF) RSD% of the 19 analytes (surrogate included) at 10 µg/L were in the range of 1.6 to 4.5%. RF RSD% at 50 µg/L was less than 2.5%, demonstrating excellent instrument repeatability for quantitation analysis with high confidence.

The linearity evaluation was based on the relative response factor (RRF) RSD% of 18 PCBs across the six calibration levels. The RRF RSD% of 18 analytes and one surrogate from 10 to 500 ppb were between 2.8 and 4.8% (Figure 4), well below the RRF RSD% limit of 15% as specified in HJ 743-2015. Figures 5A and 5B show two representative calibration curves for PCB 81 and PCB 180. Figure 6 shows the overlaid TIC SIM chromatograms of PCB standards from 10 to 500 µg/L. Table 4 shows the detailed repeatability and linearity results.



Target Mass	Rel. to Mass	Lower Limit %	Upper Limit %	Rel. Abn %	Raw Abn	Pass/Fail
51	198	30	60	56.9	1280	Pass
68	69	0	2	0.0	0	Pass
70	69	0	2	0.0	0	Pass
127	198	40	60	50.8	1142	Pass
197	198	0	1	1.0	22	Pass
198	198	100	100	100.0	2249	Pass
199	198	5	9	5.9	132	Pass
275	198	10	30	20.1	452	Pass
365	198	1	100	4.3	97	Pass
441	443	1E-10	100	41.0	174	Pass
442	198	40	100	98.0	2204	Pass
443	442	17	23	19.3	425	Pass

Figure 3. MSD DFTPP tune result conformity assessment.

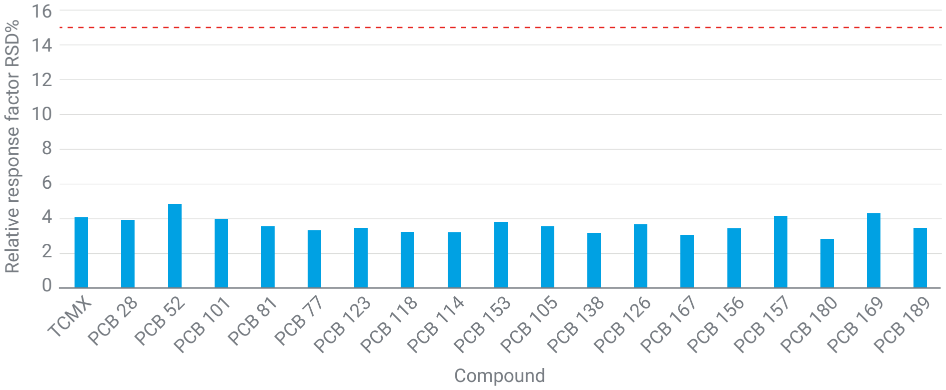


Figure 4. The RRF RSD% of 18 PCBs and TCMX across the calibration range.

Table 3. The quantifier ion and qualifier ions of 18 PCBs, surrogate, and internal standard.

Peak No.	Compounds	Congener No.	Retention Time (min)	Quantifier Ion and Qualifier Ions
1	tetrachloro-*m*-xylene/surrogate	NA	8.653	242/244/246
2	2,4,4’-trichlorobiphenyl	PCB 28	10.162	256/258/186/188
3	2,2’,5,5’-tetrachlorobiphenyl	PCB 52	10.568	292/290/222/220
4	2,2’,4,5,5’-pentachlorobiphenyl	PCB 101	11.78	326/328/254/256
5	3,4,4’,5-tetrachlorobiphenyl	PCB 81	12.262	292/290/222/220
6	3,3’,4,4’-tetrachlorobiphenyl	PCB 77	12.441	292/290/222/220
7	2',3,4,4',5-pentachlorobiphenyl	PCB 123	12.794	326/328/254/256
8	2,3’,4,4’,5-pentachlorobiphenyl	PCB 118	12.859	326/328/254/256
9	2,3,4,4’,5-pentachlorobiphenyl	PCB 114	13.061	326/328/254/256
10	2,2’,4,4’,5,5’-hexachlorobiphenyl	PCB 153	13.355	360/362/290/288
11	2,3,3’,4,4’-pentachlorobiphenyl	PCB 105	13.25	326/328/254/256
12	2,2’,3,4,4’,5’-hexachlorobiphenyl	PCB 138	13.798	360/362/290/288
13	3,3’,4,4’,5-pentachlorobiphenyl	PCB 126	14.038	326/328/254/256
14	2,3',4,4',5,5'-hexachlorobiphenyl	PCB 167	15.03	360/362/290/288
15	2,3,3',4,4',5-hexachlorobiphenyl	PCB 156	14.41	360/362/290/288
16	2,3,3',4,4',5'-hexachlorobiphenyl	PCB 157	14.925	360/362/290/288
17	2,2’,3,4,4’,5,5’-heptachlorobiphenyl	PCB 180	15.274	394/396/324/326
18	3,3',4,4',5,5'-hexachlorobiphenyl	PCB 169	15.821	360/362/290/288
19	2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB 189	16.806	394/396/324/326
20	2,2’,4,4’5,5’-hexabromobiphenyl/IS	PBB 153	19.642	308/310/468

Table 4. Instrument repeatability, linearity, limit of detection (LOD), and method recovery rate.

Compound	Repeatability		RRF RSD% for Linearity	Instrument LOD (µg/L)	Method LOD (µg/kg)	Recovery Rate (Spiked Quartz sand)	Recovery Rate (Spiked soil)
	10 µg/L	50 µg/L					
TCMX	1.6%	1.5%	4.17%	0.81	0.081	85.9%	74.3%
PCB 28	2.7%	1.5%	4.04%	0.38	0.038	87.8%	81.8%
PCB 52	1.7%	1.7%	4.85%	0.61	0.061	85.8%	87.9%
PCB 101	1.7%	2.1%	4.00%	0.99	0.099	94.1%	94.9%
PCB 81	2.9%	2.3%	3.64%	0.74	0.074	95.0%	88.6%
PCB 77	2.8%	2.2%	3.31%	0.95	0.095	94.7%	72.0%
PCB 123	2.6%	1.8%	3.52%	1.05	0.105	93.3%	87.3%
PCB 118	3.7%	2.5%	3.24%	0.89	0.089	88.0%	96.7%
PCB 114	2.9%	1.9%	3.23%	1.76	0.176	96.9%	81.9%
PCB 153	1.9%	1.7%	3.92%	1.60	0.160	91.0%	84.6%
PCB 105	1.8%	2.0%	3.57%	1.27	0.127	96.7%	93.7%
PCB 138	1.9%	1.5%	3.18%	1.42	0.142	97.2%	102.8%
PCB 126	4.5%	2.5%	3.68%	1.44	0.144	99.1%	91.5%
PCB 167	3.2%	2.1%	3.16%	1.57	0.157	98.5%	87.8%
PCB 156	4.1%	1.8%	3.43%	1.31	0.131	102.0%	81.9%
PCB 157	2.7%	1.4%	4.29%	1.44	0.144	95.9%	74.1%
PCB 180	3.2%	1.4%	2.84%	2.73	0.273	99.1%	103.2%
PCB 169	4.1%	2.5%	4.34%	2.02	0.202	101.4%	72.5%
PCB 189	2.9%	2.2%	3.44%	2.92	0.292	103.4%	103.8%

The method recovery rate was assessed by analysis of 10 g of spiked blank quartz sand at 2 µg/kg and spiked soil sample at 1 µg/kg. The sample handling and extraction process followed the HJ 743-2015 method. The recovery rate for 18 analytes and one surrogate in blank quartz sand were from 85.6% to 103.4%. The recovery rate for spiked soil matrix was from 72% to 103.8%. The test results located well within the recovery rate range of 60% to 130% for the spiked soil sample required in HJ 743-2015. Figure 7 shows the chromatograms of soil matrix and spiked soil matrix.

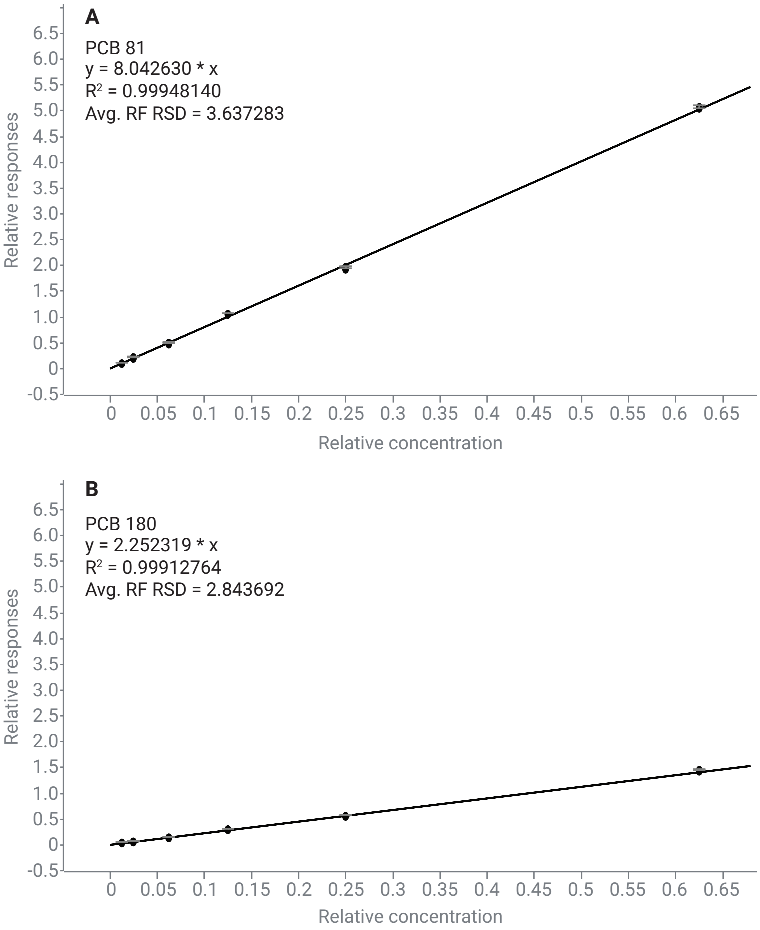


Figure 5. (A) Calibration curve of PCB 81. (B) Calibration curve of PCB 180.

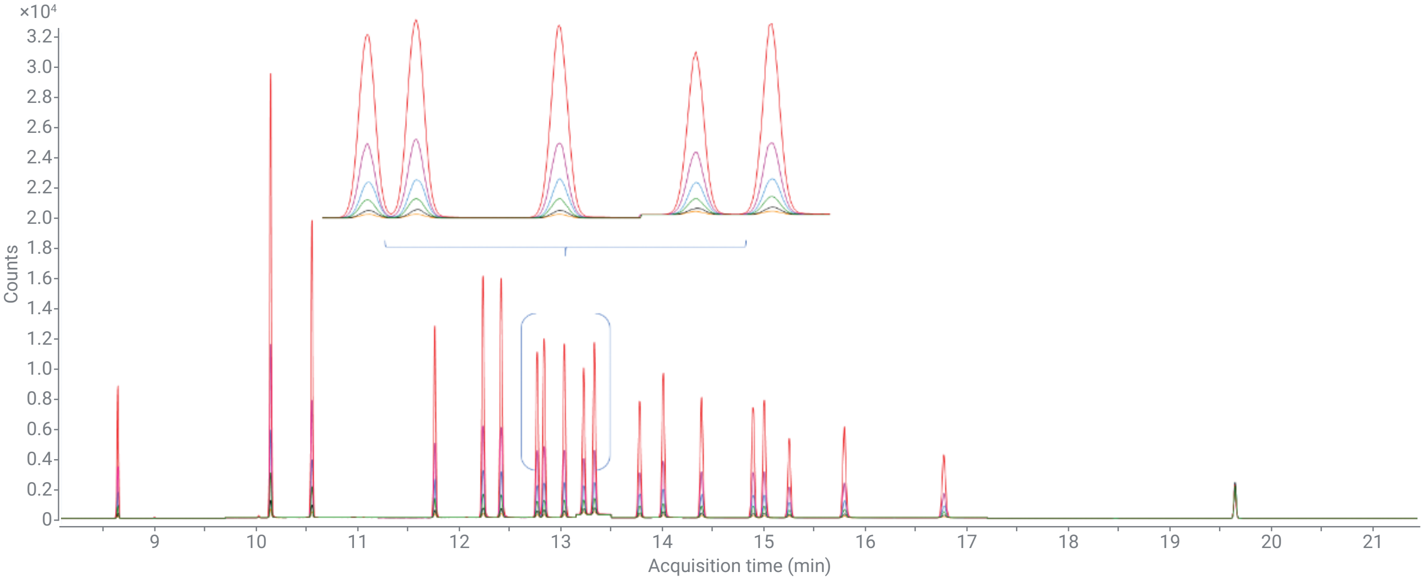


Figure 6. Overlaid TIC SIM of the 18 PCBs mixture across the six calibration levels.

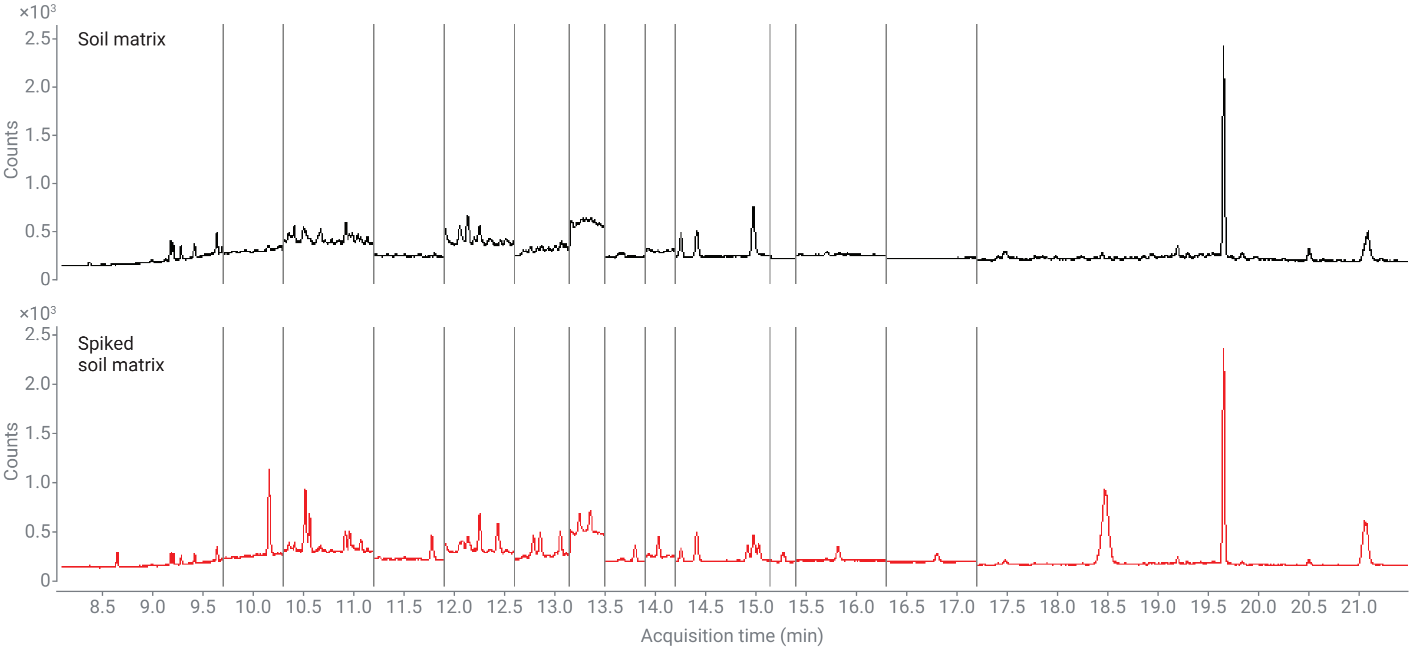


Figure 7. TIC SIM chromatograms of soil matrix and spiked soil sample.

The instrument LOD for the 18 PCBs, generated at a signal-to-noise ratio (S/N) of 3:1, were calculated based on the S/N of a 10 µg/L calibration standard. Method HJ 743 recommends that 5 to 15 g of soil or sediment are extracted and concentrated in 1 mL of hexane for GC/MS analysis. Following this guidance, the calculated instrument LOD of 1 µg/L PCB can be translated into the method LOD of 0.1 µg/kg PCB in 10 g of sample. Table 4 lists the estimated method LOD under the premise that 10 g of real sample are extracted and concentrated in 1 mL of hexane for analysis. The calculated method LOD is in the range of 0.04 to 0.3 µg/kg, better than the requirement of 0.4 to 0.6 µg/kg in HJ 743-2015 standard. This can be used as a reference to understand the capability of the 8890 GC/5977B GC/MSD platform for the measurement of PCBs in real samples.

Conclusion

This Application Note has applied the 8890 GC/5977B GC/MSD to PCB analysis in soil by following the HJ 743-2015 method. The instrument performance in terms of repeatability, linearity, and LOD were investigated based on calibration standards. The area precision was from 1.5 to 4.5% depending on sample concentration. The RRF RSD% of 18 PCBs from 10 to 500 µg/L were less than 5%, demonstrating excellent linearity across the calibration range. Instrument detection limits for 18 PCBs were from 0.4 to 3.0 µg/L, which can be translated into 0.04 to 0.3 µg/kg in real sample. The recovery result from spiked blank quartz sand and soil sample showed the effectiveness of sample handling process in HJ 743-2015 standard. The above-mentioned test results demonstrate the excellent repeatability and sensitive detection of the 8890 GC/5977B GC/MSD system, which satisfactorily meets or exceeds the requirement of HJ 743-2015 standard and proves that the tested system can provide trusted analysis for PCBs in soil and sediment matrix.

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