

Improving Sample Preparation and Analysis for Organochlorine Pesticides Using an Optimized Extraction and Analytical Technique

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Abstract

Although organochlorine pesticides have been banned for more than half a century in some cases, their prevalence and persistence in the environment ensure that the necessity of monitoring for them continues well into the future. Due to the periodic influx of samples, environmental labs are oftentimes faced with a large quantity of samples to prepare and analyze with a limited time with which to complete the task. In addition to this, the cost of performing the work sometimes may exceed the revenues generated and therefore, a more cost effective solution would be welcomed by those in such a dilemma.

In this presentation, a methodology is introduced that is designed specifically to significantly reduce the time and cost associated with preparing and analyzing organochlorine pesticide samples. What this means for the laboratory is less time invested in each individual sample, ultimately leading to higher sample throughput and less cost invested.

In addition to an efficient solid phase extraction method, the use of GC oven volume reduction is utilized to increase instrument ramping capability, thereby shortening analysis time per sample. Total instrument cycle time is around ten minutes per sample, with all analytes eluting in close to five minutes, using a dual column set-up and micro-ECD detection.

Objectives

- To show the capacity of Resprep® CarboPrep Plus SPE Cartridges for the extraction of organochlorine pesticides from water.
- To illustrate the low background of extractable material from the cartridge and how it compares to the level of pesticide standards.
- To demonstrate the instrument performance advantages of the Resprep® CarboPrep Plus SPE Cartridges using the specified method conditions.
- To utilize the faster oven ramp rates provided by the GC Accelerator oven insert kit to obtain faster analysis times for chlorinated pesticides. In addition, speed will be gained by the use of hydrogen carrier gas at a high linear velocity.

Extraction Materials and Method

- Resprep® CarboPrep Plus SPE Cartridges were evaluated in the format: a 3 mL, 95 milligram (cat.# 25659)
- An Agilent 7890 GC-μECD with autosampler was used for this work
- Reference standards used are as follows: tetrachlorometaxylyene, (cat.# 32027), decachlorobiphenyl, (cat.# 32029), hexachlorobenzene, (cat.# 32231), Organochlorine Pesticide Mix, (cat.# 32292)
- Samples were prepared and processed by spiking 100 mL DI water that had been treated with 100 mg/L sodium sulfite, acidified to pH >2 with HCl, and 2 mL methanol, with a spike solution containing 23 compounds to achieve a concentration of 8 – 16 ppb.
- Cartridges were conditioned by applying ethyl acetate, dichloromethane, methanol, and DI water in series and attaching a Sample Delivery System (cat.# 26250) to the cartridges and the sample bottles with sample being loaded at 10 mLs/min.
- Upon sample transfer completion, the cartridges were dried at full vacuum for 10 mins followed by elution using ethyl acetate to collect 25 mL of eluate.

Results and Discussion

- Although good recoveries were observed at the concentrations illustrated 8/16 ppb (Figure 1a, Table 1), additional work remains in providing better transfer of pesticides at lower concentrations to the cartridge as this has been identified as a step where losses of the more volatile pesticides are incurred at lower levels (Figure 1b).
- Some of the advantages to converting to SPE extraction over separatory funnel LLE are overall time savings, much less labor intensive, large reduction in solvent volumes resulting in cost saving for both purchase and waste removal and solvent concentration, more amenable to automation, requires less hood space.
- The GC Accelerator Oven Insert kit reduces total oven volume, therefore increasing the maximum achievable oven ramping rate.
- Using the GC Accelerator and an optimized method, all chlorinated pesticides elute in close to 5 minutes on both the Rtx-CLPesticides and Rtx-CLPesticides2 columns (Figure 5). Total cycle time is ~10 minutes per sample.
- In addition to taking advantage of faster ramp rates, hydrogen carrier gas was used at a high linear velocity to further decrease analysis time.

Figure 1a. Illustrates the recoveries of analytes at 8 – 16 ppb relative to a recovery standard

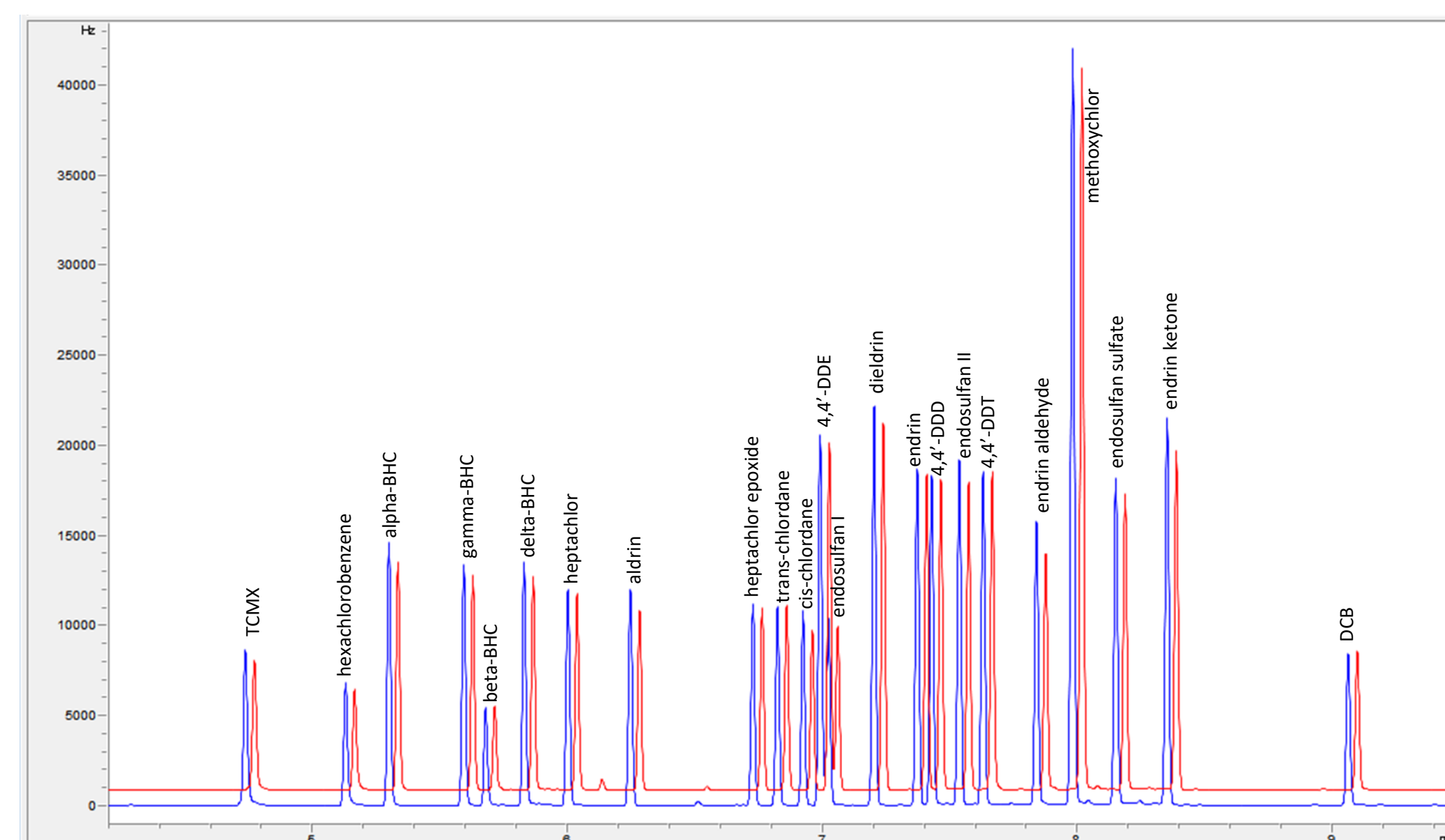
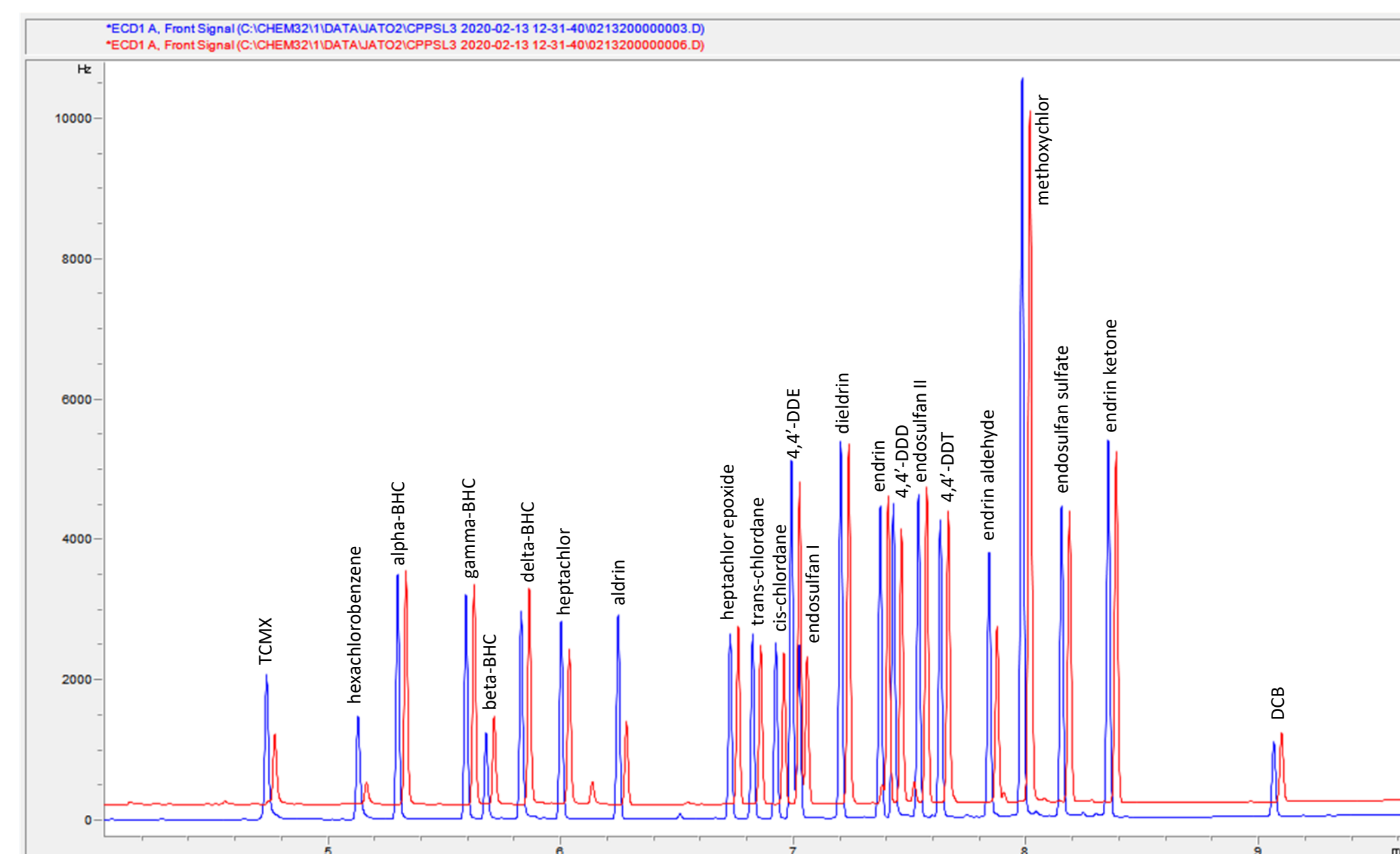


Figure 1b. Illustrates the recoveries of analytes at 2 – 4 ppb relative to a recovery standard



Analytical Conditions:

Column: Rtx-CLPesticides, 30 m x 0.32 mm ID x 0.32 μm
Injection Volume: 2 μL, pulsed splitless
Liner: Topaz 4.0 mm ID single taper w/wool (cat.# 23303)
Injection Temperature: 250°C
Purge Events: 50 mL/min @ 0.75 min
Oven Temperature: 90°C (hold 0.5 min) to 330°C @ 30°C/min (hold 2 min)
Carrier Gas: Helium, constant flow
Carrier Flow Rate: 3.0 mLs/min
Detector Temperature: 330°C
Makeup Gas: Nitrogen @ 50 mLs/min

Table 1. Recoveries obtained from a set of three spiked samples using CarboPrep Plus

Compound	Retention Time	Rec-1 (%)	Rec-2 (%)	Rec-3 (%)	Avg Rec (%)	%RSD
TCMX (surrogate)	4.74	83	90	85	86	4.3
hexachlorobenzene	5.13	84	92	85	87	5.0
alpha-BHC	5.30	87	91	84	87	4.3
gamma-BHC	5.59	87	92	84	88	4.6
beta-BHC	5.68	91	92	84	89	5.2
delta-BHC	5.82	87	92	83	87	5.1
heptachlor	6.00	91	94	87	91	3.7
aldrin	6.25	82	87	80	83	4.6
heptachlor epoxide	6.73	94	95	90	93	3.1
gamma-chlordane	6.00	90	92	86	89	3.5
alpha-chlordane	6.92	81	82	76	80	4.0
4,4'-DDE	7.00	91	92	84	89	4.8
endosulfan I	7.02	86	90	82	86	4.5
dieldrin	7.20	92	93	85	90	4.5
endrin	7.37	93	95	87	92	4.5
4,4'-DDD	7.43	91	92	87	90	3.2
endosulfan II	7.54	91	93	85	90	4.4
4,4'-DDT	7.63	95	98	91	95	3.3
endrin aldehyde	7.84	83	90	83	85	4.6
methoxychlor	7.98	94	97	90	93	3.9
endosulfan sulfate	8.15	86	92	84	87	4.7
endrin ketone	8.35	88	91	85	88	3.5
DCB (surrogate)	9.06	96	106	96	99	5.7

Figure 2. A 12-port vacuum manifold with sample delivery system was employed for the SPE extraction of pesticides



Analytical Fast Method

- Rtx-CLPesticides, 30 m x 0.32mm x 0.32 μm, (cat.# 11123-051) and Rtx-CLPesticides2, 30 m x 0.32 mm x 0.25 μm, (cat.# 11323-051) columns were obtained tied, without cages. This allows them to fit in the oven with the GC Accelerator Oven Insert kit (cat.# 23849) (Figure 3). A 5 meter Rxi guard column (cat.# 10029) was installed in the back inlet and then split into the analytical columns with a "Y" press-tight connector (cat.#20403-261).
- A GC Accelerator Oven Insert kit (cat.# 23849) was installed in Agilent 7890A with dual μECD detectors as shown in Figure 4. This kit reduces oven volume, allowing increased ramp rates.
- Instrument conditions were as follows:

Sample: Organochlorine pesticide mix AB #2 (cat.# 32292)
Pesticide surrogate mix (cat.# 32453)
Diluent: n-Hexane
Injection: 2 μL splitless (hold 0.3 min)
Liner: Topaz 4 mm ID single taper inlet liner w/wool (cat.# 23303)
Inj. Temp.: 250 °C
Purge Flow: 40 mL/min
Oven:
Oven Temp.: 120 °C (hold 0.3 min) to 200 °C at 60 °C/min to 230 °C at 25 °C/min to 320 °C at 35 °C/min (hold 1.5 min)
Carrier Gas: H2, constant flow
Linear Velocity: 100 cm/sec
Detector: Micro-ECD @ 330 °C
Make-up Gas Flow Rate: 60 mL/min
Make-up Gas Type: N2
Data Rate: 50 Hz
Instrument: Agilent 7890A GC

Figure 3. GC Accelerator Oven Insert Kit



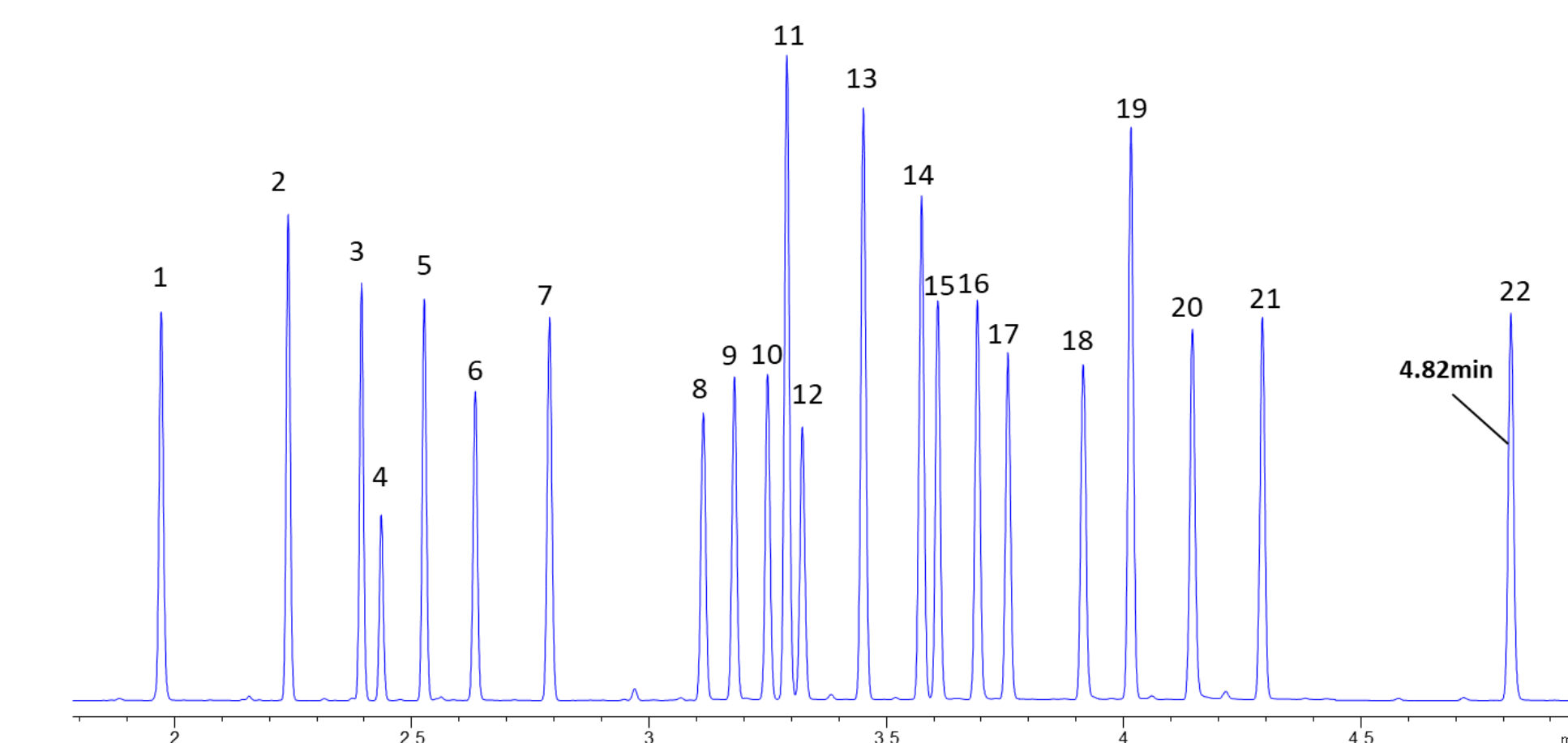
Figure 4. Installation of GC Accelerator Oven Insert Kit with dual column configuration.

- Step 1:** Install columns without cages. Guard column connects to analytical columns with "Y" press-tight.
- Step 2:** Install blocks as shown. The space to the right of the top block allows one column to reach the front detector.
- Step 3:** Install final insert. If installed correctly, oven door should close without excessive force.

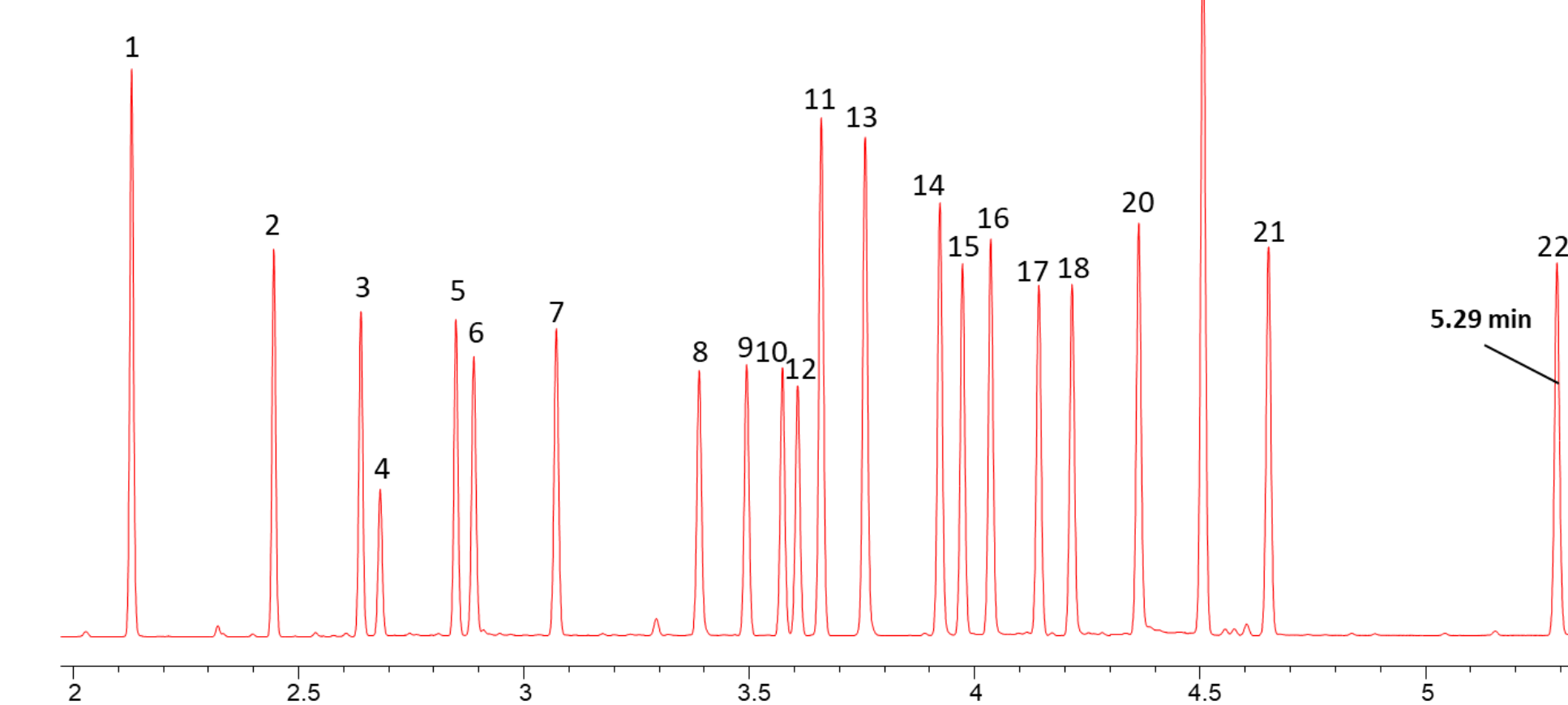


Figure 5. Fast chlorinated pesticides dual column analysis using the GC Accelerator Oven Insert kit. Conditions are listed under Analytical Fast Method section.

Rtx-CLPesticides 30m x 0.32mm x 0.32μm
Cat #: 11141-051



Rtx-CLPesticides2 30m x 0.32mm x 0.25μm
Cat #: 11324-051



1. Tetrachloro-m-xylene
2. α-BHC
3. β-BHC
4. γ-BHC
5. δ-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. trans-Chlordane
10. cis-Chlordane
11. 4,4'-DDE
12. Endosulfan I
13. Dieldrin
14. Endrin
15. 4,4'-DDD
16. Endosulfan II
17. 4,4'-DDT
18. Endrin aldehyde
19. Methoxychlor
20. Endosulfan sulfate
21. Endrin ketone
22. Decachlorobiphenyl