A New, Unique Stationary Phase for the Rapid Analysis of Organochlorine Pesticides

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Abstract

Many organochlorine pesticides are known or suspected mutagens and/or carcinogens. Due to the nature of these compounds, along with their long-term persistence in the environment, organochlorine pesticides continue to be some of the most widely monitored analytes for the environmental industry. The ability to rapidly and accurately analyze samples, without the need to invest in new, complex equipment can create a competitive advantage.

This poster discusses the use of a new, unique stationary phase for the rapid analysis of organochlorine pesticides. This phase allows a sub 10-minute analysis time for the 20 common pesticides and 2 surrogates analyzed by US EPA Method 8080. This is accomplished in the constant pressure mode, without need for constant flow or pressure pulses to achieve separation. In addition, this phase can be used in conjunction with a second stationary phase, Rtx-CLPesticides2, to create a dual column confirmation system for analyzing the 22 components in less than 10 minutes, with the two columns exhibiting differing selectivity.

Introduction

In the environmental industry, the chlorinated pesticides analytical methods often are the most challenging to perform. Analysts struggle with linearity, breakdown, and lengthy calibrations; as well as column bleed, column reactivity and poor separation. Advancements have been made to address these issues with the development of new columns that are designed specifically for the separation of chlorinated pesticides, to be used in parallel for simultaneous quantification and confirmation by gas chromatography/electron capture detection (GC/ECD). This paper will show applications using the new Rtx-440 column with three different confirmation columns. The advantages and disadvantages will be discussed with each column pair.

The three column pairs evaluated:

1.) Rtx-440 & Rtx-XLB

2.) Rtx-440 & Rtx-CLPesticides

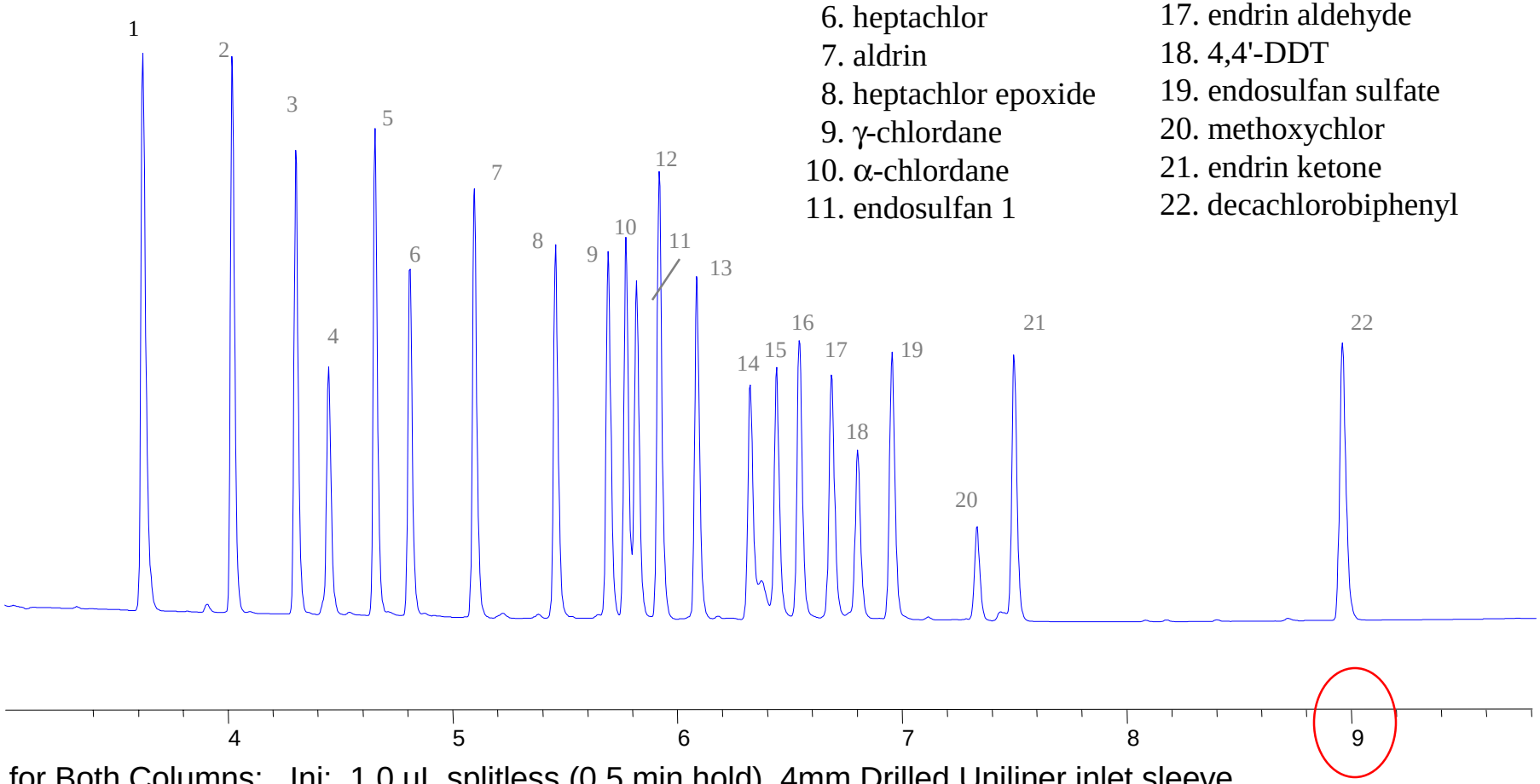
3.) Rtx-440 & Rtx-PCB

Rtx-440 & Rtx-XLB: Low Bleed and Excellent Resolution in Less Than 12 Minutes (Figures 1a & 1b).

Decachlorobiphenyl elutes off of the “XLB” phase in 11.5 minutes, while the target compounds listed in EPA Method 8080 are 80% resolved on both columns. Optimization of the expanded list of compounds found in EPA Method 8081A resulted in 80% resolution of the 32 target compounds (plus the surrogates) on the Rtx-440, with the exception of kepone and endrin aldehyde. The Rtx-XLB phase under the same conditions has two poorly resolved pairs: endrin/2,4’-DDT & endosulfan II & kepone. The clear advantage of this column pair is the rapid analysis and low bleed without a sacrifice in resolution. These columns have the same elution order for the EPA 8080 pesticides, which is a disadvantage of this application. Although there are elution order differences for the expanded list and the retention times are different for all of the chlorinated pesticides there is still a need to find a more dissimilar stationary phase as a confirmation column.

Figure 1a: Rtx-440 30m x 0.32mm, 0.50µm
cat#12939

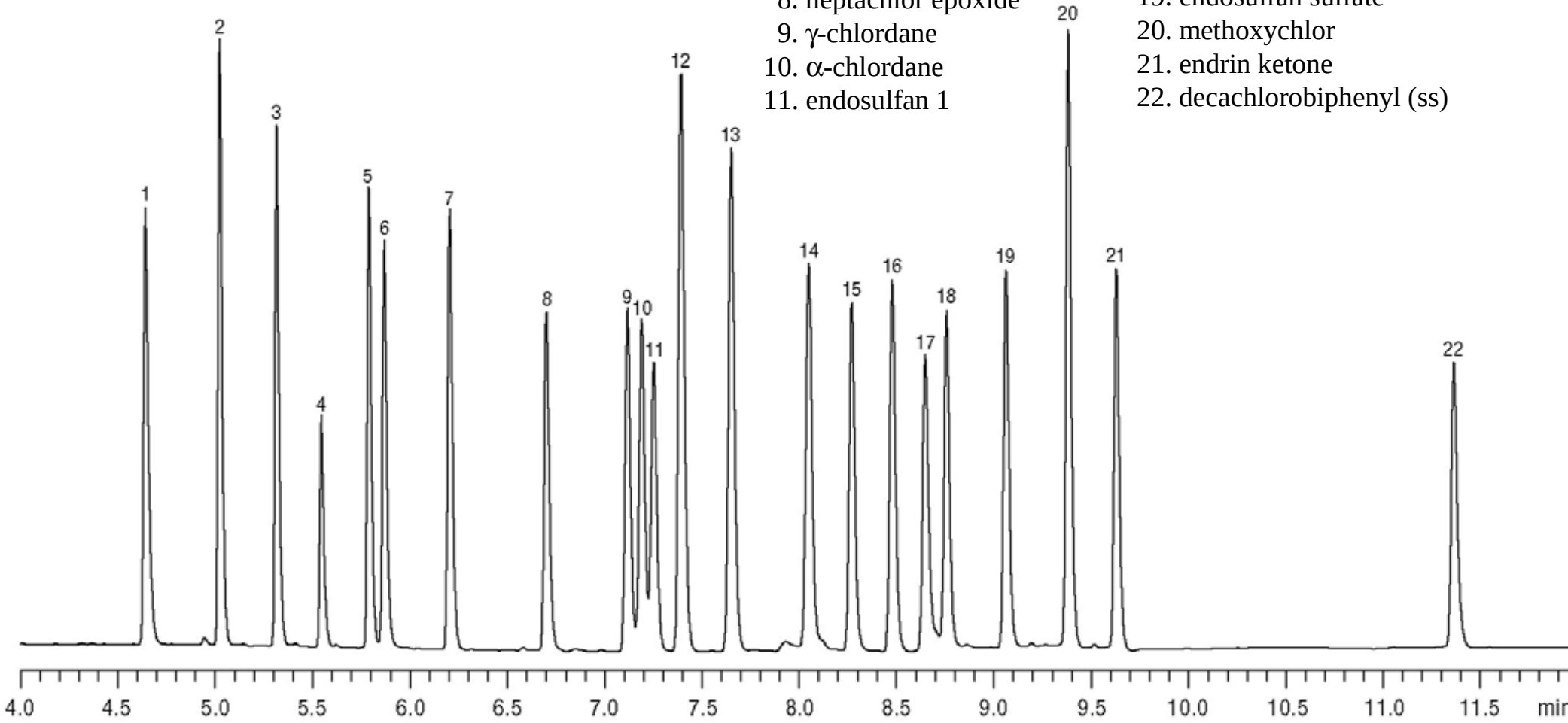
1. TCX
2. α-BHC
3. γ-BHC
4. β-BHC
5. δ-BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9. γ-chlordane
10. α-chlordane
11. endosulfan 1
12. 4,4’-DDE
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endolsulfan II
17. endrin aldehyde
18. 4,4'-DDT
19. endosulfan sulfate
20. methoxychlor
21. endrin ketone
22. decachlorobiphenyl



Conditions for Both Columns: Inj: 1.0 uL splitless (0.5 min hold), 4mm Drilled Uniliner inlet sleeve
Inj. Temp: 225°C Carrier gas: hydrogen, constant pressure, 71cm/sec @ 140°C
Oven temp: 140°C(0.5min) to 268°C @ 30°C/min (0min), to 290°C @ 11°C/min (0min), to 330°C @ 25°C/min (5min)

Figure 1b: Rtx-XLB 30m x 0.32mm, 0.50µm film cat#12839

1. TCX
2. α-BHC
3. γ-BHC
4. β-BHC
5. δ-BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9. γ-chlordane
10. α-chlordane
11. endosulfan 1
12. 4,4’-DDE
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endolsulfan II
17. endrin aldehyde
18. 4,4'-DDT
19. endosulfan sulfate
20. methoxychlor
21. endrin ketone
22. decachlorobiphenyl (ss)



Rtx-440 & Rtx-CLPesticides2 Columns: A Sub-10-Minute Analysis Time (figures 2a & 2b).

Figure 2a shows a separation of 20 commonly analyzed organochlorine pesticides obtained in less than 10 minutes by using an Rtx-440 column. Only alpha-chlordane and endosulfan I (peaks 10 & 11) are not separated to baseline. The advantage of this column pair is the difference in selectivity. This Rtx-CLPesticides2 column when run under the given conditions (figure2b) that achieve a sub-7-minute analysis time result in 60% resolution versus the 80% peak resolution of the Rtx-440/Rtx-XLB pair. The column exhibits good thermal stability as indicated by the baseline between the initial temperature and the maximum temperature of the program, 330°C. In a dual-column approach to this application, an Rtx-440 column can be paired with an Rtx-CLPesticides2 column. The latter column will provide an equally fast separation (figure 2b) and near equivalent resolution, with a reverse in elution order for endrin aldehyde and 4,4'-DDT (peaks 17 &18).

Figure 2a: Rtx-440 30m x 0.32mm, 0.50µm

1. TCX
2. α-BHC
3. γ-BHC
4. β-BHC
5. δ-BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9. γ-chlordane
10. α-chlordane
11. endosulfan I
12. 4,4'-DDE
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endosulfan II
17. endrin aldehyde
18. 4,4'-DDT
19. endosulfan sulfate
20. methoxychlor
21. endrin ketone
22. decachlorobiphenyl

Conditions for both columns:
Inj.: 1.0µL splitless (hold 0.75 min.), 4mm Drilled Uniliner® inlet liner (cat.# 21055)
Inj. temp.: 225°C Det.: ECD @ 320°C
Carrier gas: hydrogen, constant pressure
Linear velocity: 73cm/sec. @ 140°C
Oven temp.: 140°C (hold 0.5 min.) to 268°C @ 30°C/min., to 290°C @ 11°C/min., to 330°C @ 25°C/min. (hold 5 min.)

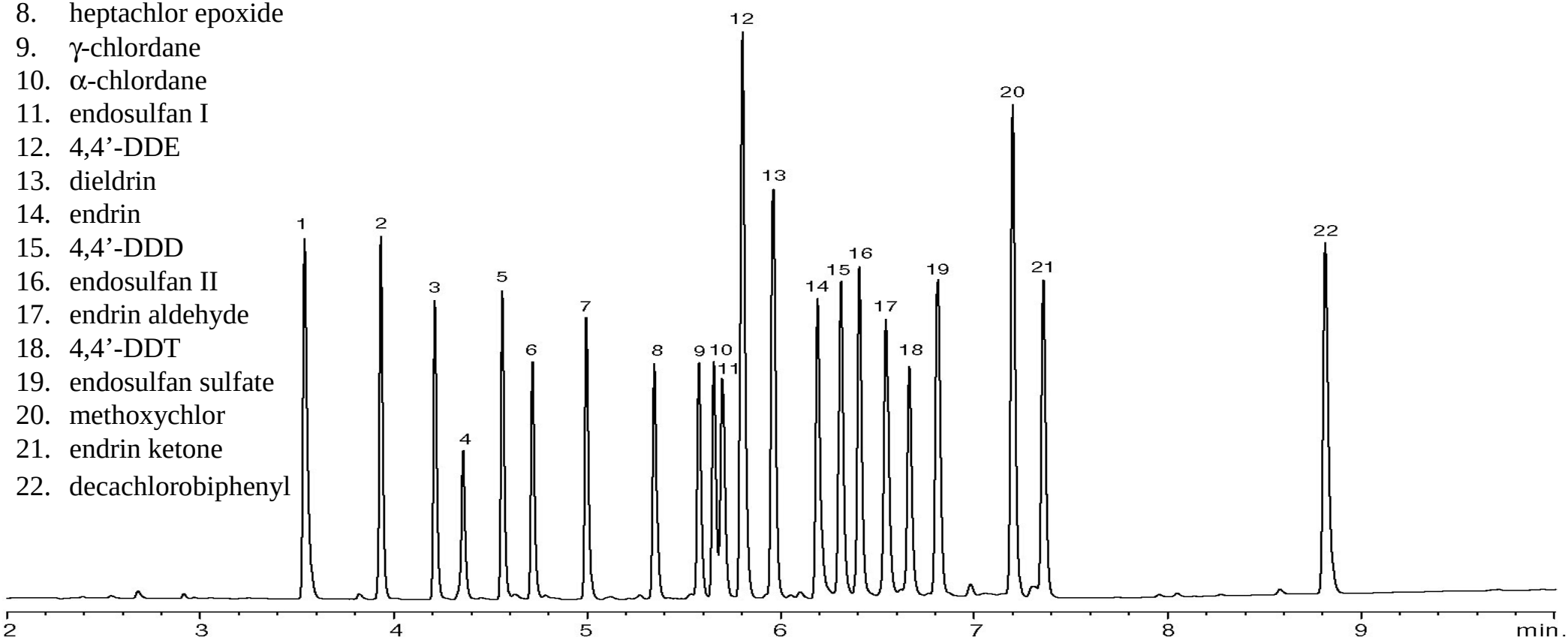
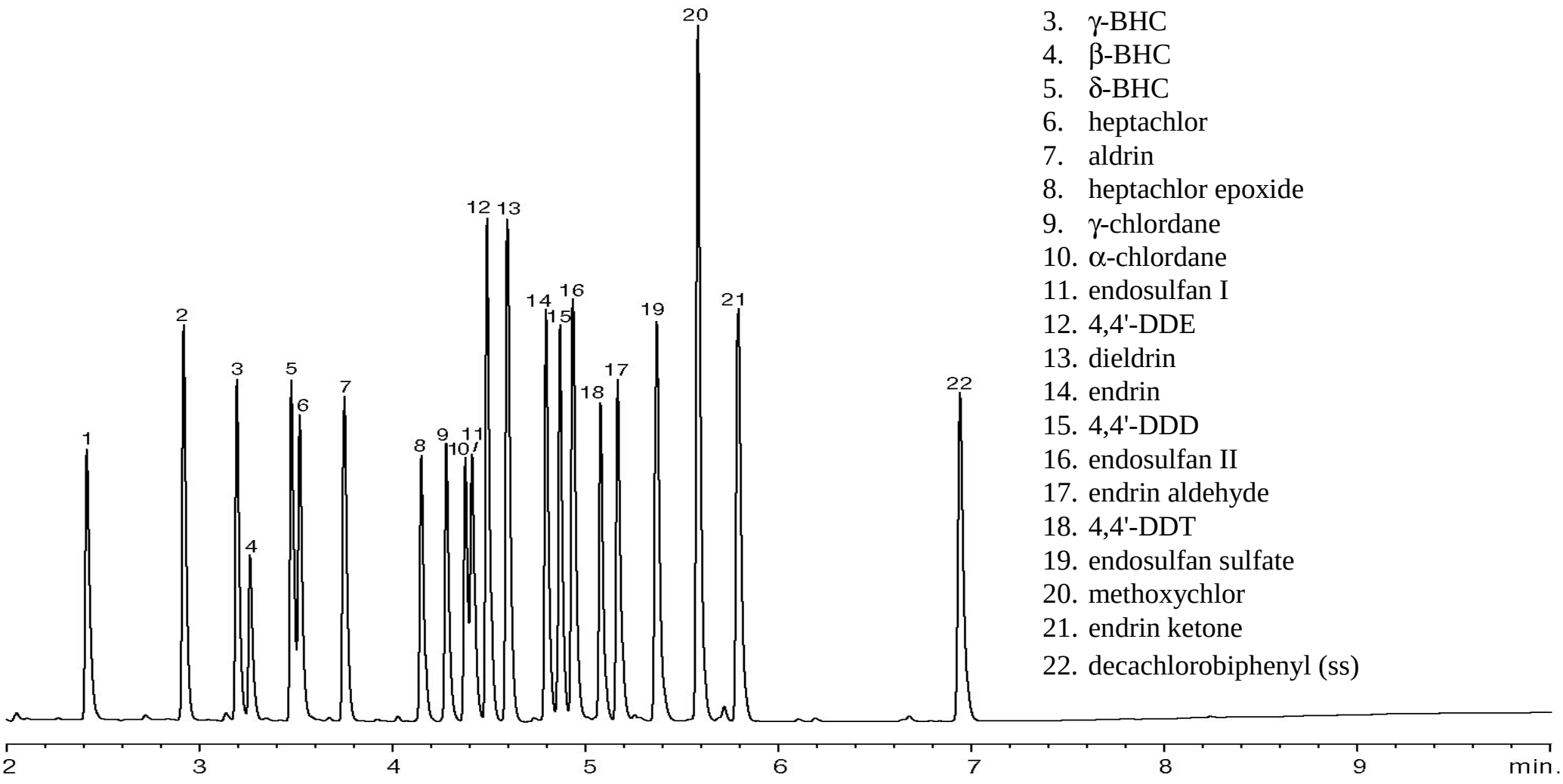


Figure 2b: Rtx-CLPesticides 30m x 0.32mm, 0.25µm Cat#11324



1. 2,4,5,6-tetrachloro-m-xylene (ss)
2. α-BHC
3. γ-BHC
4. β-BHC
5. δ-BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9. γ-chlordane
10. α-chlordane
11. endosulfan I
12. 4,4'-DDE
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endosulfan II
17. endrin aldehyde
18. 4,4'-DDT
19. endosulfan sulfate
20. methoxychlor
21. endrin ketone
22. decachlorobiphenyl (ss)

Rtx-440 & Rtx-PCB Columns: Two New Low Bleed Columns with Unique Selectivity (figures 3a & 3b).

This column pair allows the accurate determination of organochlorine pesticides or polychlorinated biphenyls (PCBs). The Rtx-PCB column is well suited for congener-specific analysis where greater PCB information is necessary versus the more commonly performed Arochlor test. The analysis of the 20 chlorinated pesticides is shown in less than 12 minutes but separation is the least optimal of the choices presented in this paper. This column pair can produce 80% resolution for EPA Method 8080 with a longer runtime (20 minutes). The selectivity between these columns is unique; there are two column pair changes: heptachlor/d-BHC (peaks 5/6) & 4,4'-DDT/endrin aldehyde (peaks 17/18). These two columns also have excellent bleed characteristics minimizing detector contamination, prolonging intervals between cleanings and thus increasing throughput over time.

Figure 3a: Rtx-440 30m x 0.32mm, 0.50µm

1. TCX
2. a-BHC
3. g-BHC
4. b-BHC
5. d-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. g-Chlordane
10. a-Chlordane
11. Endosulfan I
12. 4,4' -DDE
13. Dieldrin
14. Endrin
15. 4,4' -DDD
16. Endosulfan II
17. Endrin aldehyde
18. 4,4' -DDT
19. Endosulfan sulfate
20. Methoxychlor
21. Endrin ketone
22. Decachlorobiphenyl

Conditions for both columns:
Sample: 1mg/mL standard (cat.# 32291) & (cat#32000), 50ng/mL hexane
Inj.: 1.0µL splitless (hold 0.75 min.), custom Siltek splitless inlet liner
Inj. temp.: 250°C Det.: ECD @320°C
Carrier gas: hydrogen, constant pressure
Linear velocity: 64cm/sec. @ 100°C
Oven temp.: 140°C (0.5min.) to 268°C @30°C/min. to 290°C @11°C/min. to 330°C @25°C/min. (5min.)

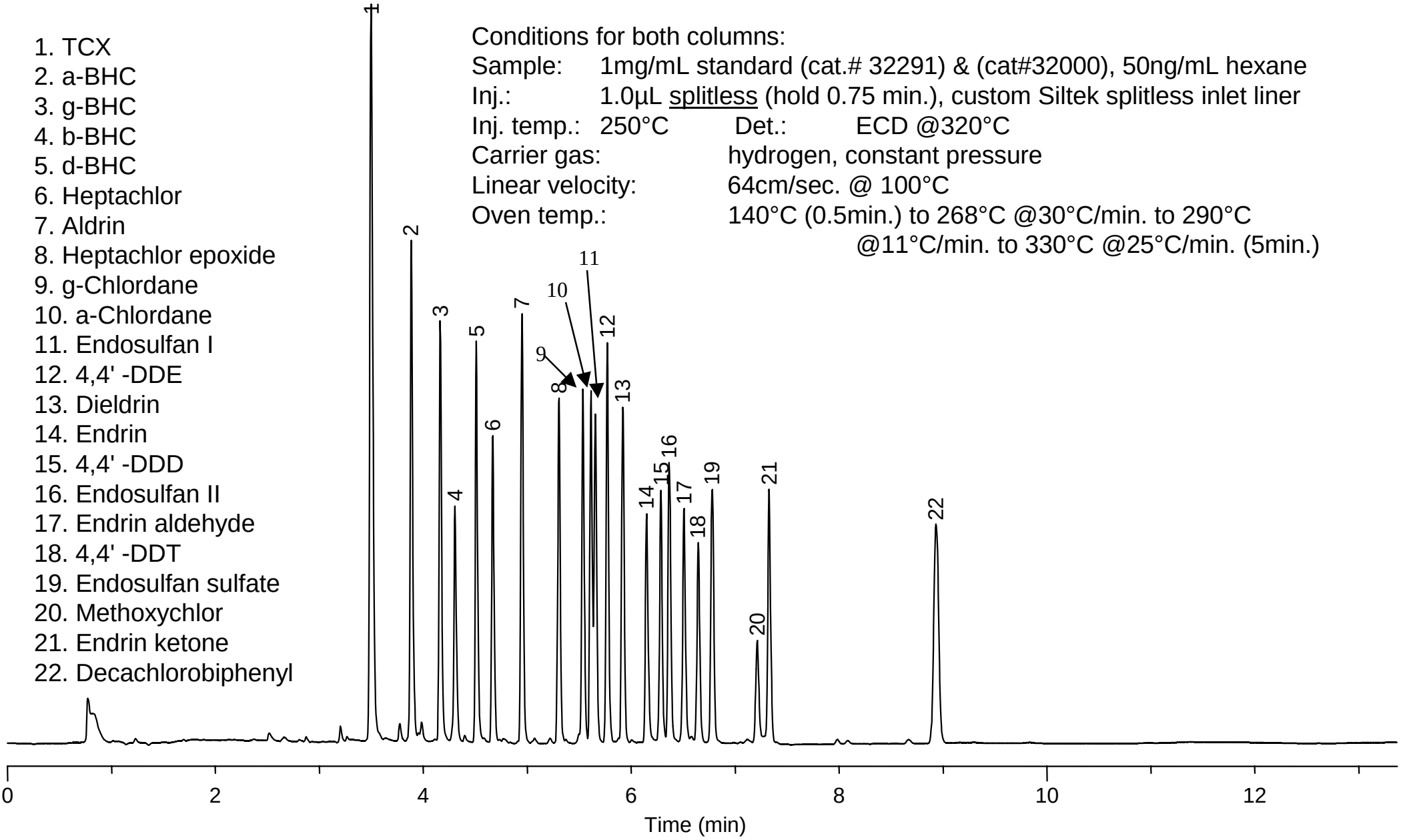
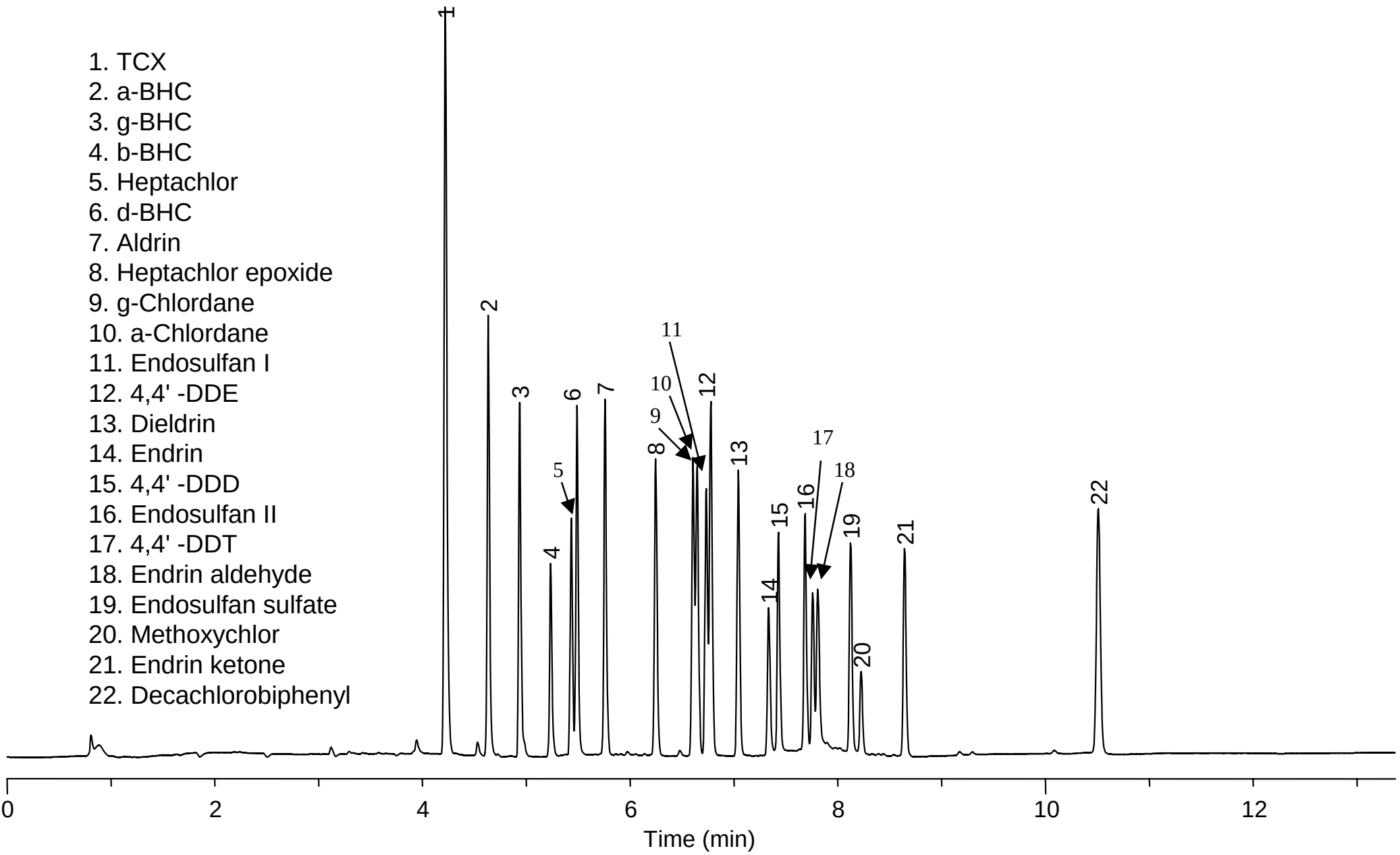


Figure 3b: Rtx-PCB 30m x 0.32mm, 0.50µm (Cat# 13239)



Conclusion

Although the analysis of chlorinated pesticides historically has been one of the more difficult tests performed by environmental testing laboratories, using any combination of the above columns for EPA pesticide methodologies will improve laboratory results and increase throughput. Laboratories using cyanopropyl-phase or phenyl-phase columns must calibrate using 5-point curves, injecting mix A and mix B compounds separately because target compounds coelute. Since there are no coelutions using the columns presented the mixes can be combined. This eliminates the need for 5 injections per calibrations and will free up a minimum of 2.5 hours a day to analyze more samples.

Three confirmation columns were examined in this paper: Rtx-XLB, Rtx-CLPesticides2 and the Rtx-PCB. The Rtx-XLB provides excellent resolution, but lacks differences in retention order to the primary column. The Rtx-CLPesticides2 has a reverse in elution order between endrin aldehyde and 4,4'-DDT with nearly equivalent resolution to the Rtx-440 primary column. The Rtx-PCB column exhibits two compound retention order changes but lacks the resolution of the Rtx-CLPesticides2 & Rtx-XLB. The Rtx-440 easily resolves the 20 chlorinated pesticides in less than 10 minutes. Determining the best confirmation column is a matter of preference. The information presented in this paper will allow laboratories to make informed decisions based upon the requirements of their clients and their specific methods.