Rapid Dual GC Column Analysis of Pesticides and Herbicides, Using Two Unique Stationary Phases

Jason Thomas, Chris English, and Gary Stidsen

Restek Corporation, 110 Benner Circle, Bellefonte, PA. 16823

Abstract

Analysis of organochlorine pesticides and acid herbicides have become a routine assay in the environmental sector. Although these pesticides were phased out decades ago they are still found in the environment. Environmental laboratories are expected to rapidly analyze contaminated extracts without sacrificing target compound identification. This test requires a gas chromatographic stationary phase with good selectivity and high thermal stability.

This poster will focus on the use of two unique stationary phases to perform a variety of EPA methods for pesticides, including 608, 8080, 8151A, and 8081A, as well as other compounds of interest. The dual column/ECD configuration allows simultaneous determination and confirmation of monitored compounds, while taking advantage of the greater sensitivity of the ECD with respect to GC/MS. Differing selectivity, and the stable nature of the two stationary phases, enable a wide variety of pesticides and herbicide analyses to be performed with this system. A single instrument can be used for several methods, eliminating the need to change columns or dedicate multiple instruments to specific analyses.

Objective

The objective of this work was to analyze several common EPA methods using the Rtx-CLP2 and Rtx-440 in a dual column configuration. The goal was to conduct the assays in under 12 minutes, if possible, with the best possible resulting resolution. This is potentially a challenging endeavor considering the variety in the compound lists of some of the various methods. The oven temperature programs and column flow rates were optimized theoretically using a modeling software. It was felt that this would help eliminate a lot of wasted effort and be the best way to realize the maximum potential of the columns.

Procedure

All chromatograms were generated using a Shimadzu 2010 GC equipped with an ECD and controlled by GC Solutions software. Each set of GC operating parameters was determined by the computer generated solution that best resolved the components contained in that particular method within a specified analysis time. The parameters were optimized first to obtain complete baseline resolution, where possible, for the Rtx-440 as the primary column, with the best resulting resolution on the Rtx-CLP2 using the same program. A 4 meter piece of 0.32mm Siltek guard column (cat.# 10027) was used, coupled to a 30m x 0.32mm x 0.5µm Rtx-440 (cat.# 12939) and a 30m x 0.32mm x 0.5µm Rtx-CLP2 (cat.# 11325) using a SeCureY connector (cat.# 20277).

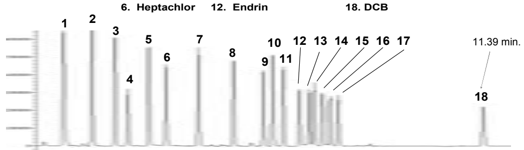
Conditions Common to all Methods:
Linear Velocity: 50cm/sec @ 140°C
Constant Pressure
Detector: Shimadzu Dual ECD
Injection Port: 275°C

Method 608: 140°C(1min) 30°C/min to 240°C(2min) 30°C/min to 330°C (4min)
Method 8080: 110°C(0.5min) 25°C/min to 230°C(0min) 15°C/min to 330°C (1min)
Method 8151A: 60°C(2min) 30°C/min to 190°C(2min) 35°C/min to 315°C (6min)
Method 8081A: 140°C(1min) 30°C/min to 240°C(2min) 30°C/min to 330°C (4min)

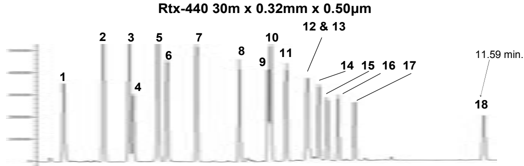
EPA Method 608

Components in EPA Method 608

1. 2,4,5,6-TCX
2. Alpha-BHC
3. Gamma-BHC
4. Beta-BHC
5. Delta-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. Endrosulfan I
10. 4,4'-DDE
11. Dieldrin
12. Endrin
13. 4,4'-DDD
14. Endosulfan II
15. Endrin Aldehyde
16. 4,4'-DDT
17. Endosulfan Sulfate
18. DCB



Rtx-440 30m x 0.32mm x 0.50µm

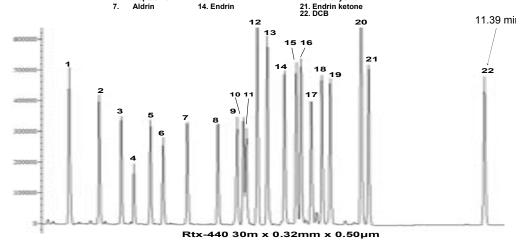


Rtx-CLPII 30m x 0.32mm x 0.50µm

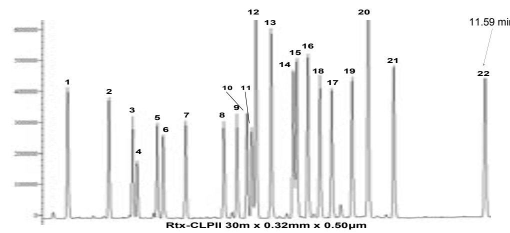
EPA Method 8080

Components in EPA Method 8080

1. 2,4,5,6-TCMX
2. Alpha-BHC
3. Gamma-BHC
4. Beta-BHC
5. Delta-BHC
6. Heptachlor
7. Aldrin
8. Hepatchlor epoxide
9. Gamma-chlordane
10. Alpha Chlordane
11. Endolsulfan I
12. 4,4'-DDE
13. Dieldrin
14. Endrin
15. 4,4'-DDE
16. Endosulfan II
17. Endrin aldehyde
18. 4,4'-DDT
19. Endosulfan sulfate
20. Methoxychlor
21. Endrin ketone
22. DCB



Rtx-440 30m x 0.32mm x 0.50µm

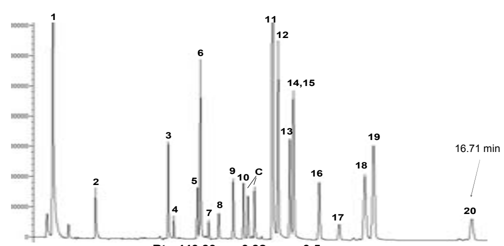


Rtx-CLPII 30m x 0.32mm x 0.50µm

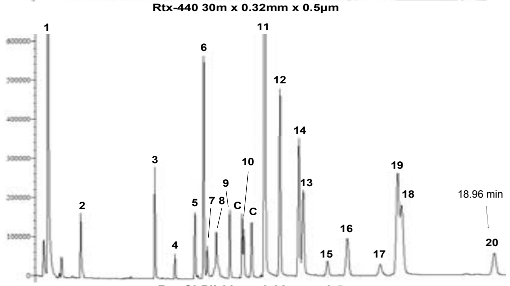
EPA Method 8151

Component List for EPA Method 8151A

1. Dalapon ME
2. 1,4-dichlorobenzene
3. 3,5-dichlorobenzoic acid ME
4. 4-nitroanisole
5. DCAA ME
6. Dicamba ME
7. MCPP ME
11. Pentachloroanisole
12. 2,4,5-TP ME
13. Chloramben ME
14. 2,4,5-T ME
15. 2,4-DB ME
16. Dinoseb ME
17. Bentazon ME



Rtx-440 30m x 0.32mm x 0.5µm

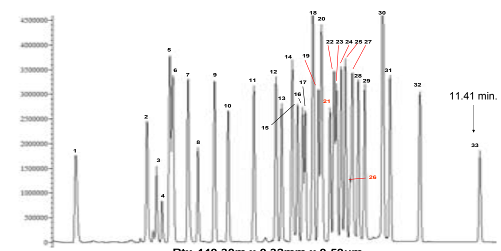


Rtx-CLPII 30m x 0.32mm x 0.5µm

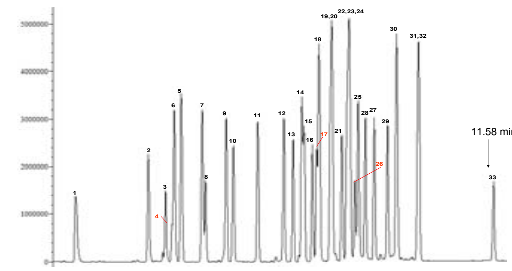
EPA Method 8081A

Components in EPA Method 8081A

1. Hexachlorocyclopentadiene
2. 2,4,5,6-TCMX
3. cis-diallate
4. trans-dialate
5. Alpha-BHC
6. Hexachlorobenzene
7. Gamma-BHC
8. Beta-BHC
9. Delta-BHC
10. Heptachlor
11. Aldrin
12. Isodrin
13. Heptachlor epoxide
14. 2,4'-DDE
15. Gamma-chlordane
16. Alpha-chlordane
17. Endosulfan I
18. 4,4'-DDE
19. 2,4'-DDD
20. Dieldrin
21. Chlorobenzilate
22. Endrin
23. 2,4'-DDT
24. 4,4'-DDD
25. Endosulfan II
26. Kepone
27. Endrin aldehyde
28. 4,4'-DDT
29. Endosulfan sulfate
30. Methoxychlor
31. Endrin ketone
32. Mirex
33. Decachlorobenzene



Rtx-440 30m x 0.32mm x 0.50µm



Rtx-CLPII 30m x 0.32mm x 0.50µm

Separation of Critical Pairs

For analyzing the most commonly used pesticide methods, 8080, and 608, the Rtx-440/Rtx-CLP2 pair proved to be a good choice, resulting in only a few cases where a fully resolved baseline was not obtained. Adequate resolution of target compounds in Method 8081A in under 12 minutes was not achieve for 2,4'-DDT & endosulfan I.

Method 8151A presented a problem due to a coelution of the internal standard 4,4'-dibromooctafluorobiphenyl with 2,4-D using the Rtx-CLP2 column. Both 8151A and the drinking water equivalent, 515, allow substitution of the internal standard and recommend 1,4-dichlorobenzene, which was incorporated into the standards in this analysis with no problems.

Two methods, however contained a component set that proved to be inseparable, under practical conditions, using this column pair. Method 505 is one of these; both the Rtx-440 and the Rtx-CLP2 could not separate simazine and atrazine. Most versions of method 508 also contain these two components, as well, and so can not be analyzed using these columns if simazine and atrazine are both target compounds.

Conclusion

Several pesticide and herbicide methods have been tried using the Rtx- 440/Rtx-CLP2 dual column setup in an attempt to determine the effectiveness of these columns under relatively fast run conditions, under 15 minutes. Overall they performed well, however, some compounds could not be entirely resolved using the same method on both columns because of a few similar compounds in the method list which are difficult to separate. In general though, this column pair has been found to be an effective setup for analyzing the vast majority of the most commonly monitored pesticides and herbicides.