

Analysis of Organochlorine Pesticides

Using 2D-GC with Rtx®-5 and Rtx®-200 Capillary GC Columns

by Frank Dorman, Ph.D., Director of Technical Development

- GCxGC analysis combines primary column and confirmation column results.
- Separate target compounds from co-extracted contaminants in sample extracts.
- Analyte refocusing effect increases sensitivity.
- Combination of Rtx®-5 and Rtx®-200 columns resolves all target pesticides.

By using application-specific capillary GC columns, such as our Rtx®-CLPesticides and Rtx®-CLPesticides2 columns, many laboratories analyzing organochlorine pesticides can separate all of the target compounds. But, with complex matrices, there still can be difficulties in resolving the target compounds from co-extracted interfering matrix components. Especially difficult are samples contaminated with chlorinated organic compounds, such as PCBs. Like the target analytes, these contaminants produce a signal on the electron capture detectors (ECDs)

commonly used for this application. In order to separate the target compounds from the co-extracted contaminants in many sample extracts, Restek chemists, in collaboration with colleagues at LECO Corporation, have investigated GCxGC technology.

Comprehensive GCxGC is a relatively new, exciting technique that increases chromatographic peak capacity by enabling the analyst to use two columns of differing selectivity in a single analysis. By coupling two columns in series, and

incorporating a modulation technique at the junction between the two columns (e.g., valving or cryomodulation), it is possible to get the benefit of each column, as in independent separations. This technique has been reviewed in depth by Professor John Dimandja¹, and the reader is urged to consult this reference for details. There are several manufacturers of commercial GCxGC instruments, and the technique can be adapted to conventional instrumentation.

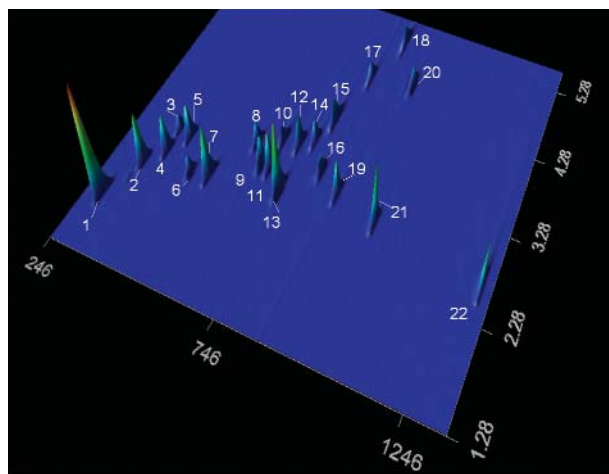
In determining which column pair to use for a GCxGC application, it is important to choose stationary phases that differ in selectivity. For this application, we choose an Rtx®-5 column for a volatility-based separation, in series with an Rtx®-200 column which is selective for halogenated compounds. The second-dimension separation from this column ensemble is focused on retention of halogenated compounds, and separates the target compounds from some of the possible interferences in the sample matrix.

Figure 1 is a GCxGC chromatogram of 22 common organochlorine pesticides, obtained from the Rtx®-5 column/Rtx®-200 column ensemble in a LECO GCxGC/ECD instrument. Table I lists the compounds and the independent retention times observed in the two dimensions of separation. By having two independent retention times, from two different columns, we obtain a primary column separation and a secondary column confirmation for the target compounds, so this technique should be in compliance with any methodology requiring a primary column/confirmation column approach.

Additionally, an analysis of a spiked extracted food sample (tomato) shows we can separate the target compounds from many co-extracted interferences (Figure 2). Recovery values for the spiked sample, listed in Table II, are in agreement with "known" values, indicating little to no matrix interference with target compound quantification, even for a difficult matrix like a food.

A secondary benefit of using cryomodulation at the column junction is peak sharpening prior to "injection" of an analyte onto the second column. This has the effect of increasing sensitivity. Due to this analyte refocusing effect, we obtained linear calibration for these compounds over a 25-fold wider range of concentration than by conventional GC. The compounds for which detection is most sensitive (e.g., the hexachlorocyclohexanes, or BHCs) normally are calibrated from 5 to 80 pg/ μ L. We were able to calibrate from 0.2 to 80 pg/ μ L, thus greatly extending the reporting limit. We also were able to employ split injection, which typically reduces injector-related problems, such as analyte adsorption and breakdown.

Figure 1 GCxGC analysis of organochlorine pesticides combines primary column and confirmation column results.



Columns: Rtx®-5 9m, 0.18mm ID, 0.20 μ m (10m column, cat.# 40201, with 1m removed)
Rtx®-200 1m, 0.18mm ID, 0.20 μ m (1m of 10m column, cat.# 45001)

Inj.: 1 μ L, split, 250°C, split ratio 50:1

Oven: Primary: 50°C (0.2 min.), 30°C/min. to 140° (no hold), 5°C/min. to 250°C (no hold)
Secondary: 50°C offset from primary oven

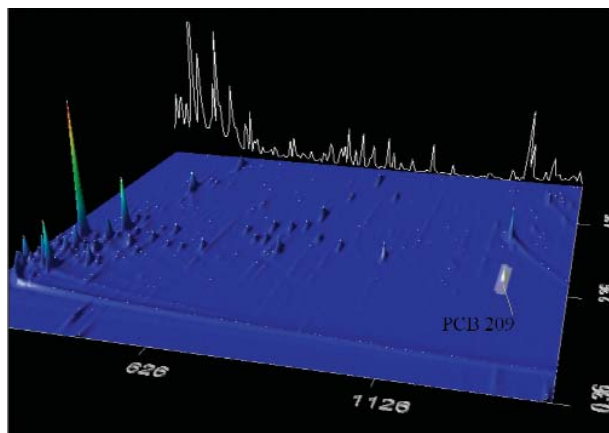
Instrument: LECO GCxGC/ECD

Modulator: Temperature offset: 30°C
Modulation time: 6 sec

Det.: ECD, 325°C, 150mL/min. nitrogen makeup gas, 50Hz

Peak identifications listed in Table I and Table II.

Figure 2 Organochlorine pesticides separated from interferences in tomato extract.



Conditions: see Figure 1

Pittcon® presentation

Jack Cochran, LECO Corporation, will present this information at the 2005 Pittsburgh Conference in Orlando, Florida. (1000-7)

For more information about this application, or about GCxGC in general, please contact our Technical Service chemists, or your Restek representative.

Reference

1. Dimandja, J., Anal. Chem. 76 (9): 167A - 174A (2004).

Acknowledgement

This investigation was conducted in collaboration with Jack Cochran, Director of Separation Science, LECO Corporation, Las Vegas, NV.

Table I Organochlorine pesticides and retention times in GCxGC separation.

Analyte	T _R (sec.)	
	Dimension 1	Dimension 2
1. tetrachloro- <i>m</i> -xylene	294	1.9
2. α-BHC	342	2.44
3. β-BHC	378	2.96
4. γ-BHC	384	2.66
5. δ-BHC	420	2.94
6. heptachlor	480	2.52
7. aldrin	534	2.58
8. heptachlor epoxide	606	3.16
9. γ-chlordane	648	2.96
10. endosulfan I	672	3.32
11. α-chlordane	678	2.96
12. dieldrin	720	3.34
13. 4,4'-DDE	732	2.72
14. endrin	756	3.46
15. endosulfan II	780	3.78
16. 4,4'-DDD	810	3.18
17. endrin aldehyde	816	4.5
18. endosulfan sulfate	864	5.2
19. 4,4'-DDT	882	2.96
20. endrin ketone	942	4.68
21. methoxychlor	1008	2.82
22. decachlorobiphenyl	1320	2.62

Table II Pesticide recovery values for a spiked sample tomato extract agree with theoretical values, indicating interference from matrix is minimal.

Analyte	Spike			
	Sample Amount Quantified	Sample Amount Quantified	Spike Amount Theoretical	Recovery (%)
1. tetrachloro- <i>m</i> -xylene	0	14.4	16	90
2. α-BHC	0	7.8	8	98
3. β-BHC	0	7.1	8	89
4. γ-BHC	0	6.8	8	85
5. δ-BHC	0	6.5	8	81
6. heptachlor	0	9.3	8	116
7. aldrin	0	7.2	8	90
8. heptachlor epoxide	0	9.3	8	116
9. γ-chlordane	0	6.9	8	86
10. endosulfan I	9.5	18.7	8	115
11. α-chlordane	0	7.5	8	94
12. dieldrin	0	17.4	16	109
13. 4,4'-DDE	0	16.8	16	105
14. endrin	0	14.2	16	89
15. endosulfan II	15.4	27.9	16	78
16. 4,4'-DDD	0	13.9	16	87
17. endrin aldehyde	0	12.8	16	80
18. endosulfan sulfate	13.1	28.2	16	94
19. 4,4'-DDT	0	15.7	16	98
20. endrin ketone	0	13	16	81
21. methoxychlor	0	76.8	80	96
22. decachlorobiphenyl	0	16.2	16	101

Rtx®-5 Column (fused silica)

(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)
Temp. limits: -60 to 325/340°C

ID	df (μm)	length	cat. #
0.18mm	0.20	10-Meter	40201

Rtx®-200 Columns (fused silica)

(Crossbond® trifluoropropylmethyl polysiloxane)
Temp. limits: -20 to 310/330°C

ID	df (μm)	length	cat. #
0.18mm	0.20	10-Meter	45001

Organochlorine Pesticide Mix AB #2

aldrin	8ug/mL	dieldrin	16
α-BHC	8	endosulfan I	8
β-BHC	8	endosulfan II	16
δ-BHC	8	endosulfan sulfate	16
γ-BHC (lindane)	8	endrin	16
α-chlordane	8	endrin aldehyde	16
γ-chlordane	8	endrin ketone	16
4,4'-DDD	16	heptachlor	8
4,4'-DDE	16	heptachlor epoxide (B)	8
4,4'-DDT	16	methoxychlor	80

In hexane:toluene (1:1), 1mL/ampul
cat. # 32292 (ea.)

Pesticide Surrogate Mix

decachlorobiphenyl
2,4,5,6-tetrachloro-*m*-xylene
200μg/mL each in acetone, 1mL/ampul
cat. # 32000 (ea.)