

Toxaphene, the Underestimated Pesticide P194

COMPOSITION OF CAMPHECHLOR

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Introduction

Despite the fact, that nowadays quantitative analysis of Toxaphene congeners in environmental samples is routine, composition of Toxaphene itself remains unknown. Direct analysis of technical product by GC gives uncertain results, because of poor resolution or complete coelution of different congeners. One of the possibilities to avoid this problem can be pre-separation of Toxaphene into several fractions on silicagel/hexane column in a hope that GC-coeluters would come out of silica gel column in different fractions. Then fractions should be analyzed separately by various methods, like GC-ECD, GC-MS or NMR¹⁾. In present article we report on the separation of Camphechlor and analysis of the fractions by GC-ECD.

Materials and Methods

Technical Toxaphene (Camphechlor 61.8%, Ehrenstorfer, E109400, lot #30302), primary st. solution of 2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB, 2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB and 2,2,5,5,8,9,9,10,10-NCB(USL-420, Promochem, certified), hexane(for residue analysis, Promochem) and silica gel(silica gel 60, 230-400 mesh, Merck) were all received from Promochem.

1.00g of Toxaphene were dissolved in 5ml of hexane and separated into 20 fractions of different volume on 70cm high, 2cm i.d. column. Elution rate – 0.6ml/min. Each fraction was analyzed upon collection, hexane evaporated off. Then fractions were dissolved in a measured volume of hexane, an aliquot taken, and internal standard (2,2,5,5,8,9,9,10,10-NCB or 2-exo,3,3,5-exo,6-endo,8,9,9,10,10-DCB) added to the aliquot in appropriate amount. An aliquot was then diluted and analyzed on GC-ECD. Conditions were as follows :

GC-Varian3700, inj. – Gerstel split/splitless at 250°C, column – DB-5(app. 50m), Det. – ECD(at 300°C), carrier gas – nitrogen, make-up – nitrogen. Pr.: 160 °C(2 min) - 20 °C/min - 280 °C(10 min) Purge 1.00-1.90 min.

For all but two compounds RRFs were postulated to be 1.00 (relative to Parl #62), for Parl#26 and Parl#50 the RRFs were determined – 1.38 and 1.10 respectively. It was shown earlier, that ECD response is rather similar for different congeners²⁾. USL-420 was a calibration standard.

Results and Discussion

1. Identification of known compounds in fractions.

We used our database of relative retention times for chlorinated terpenes^{3,4)} for assignment of peaks in each fraction. Peaks with RRTs deviation less than 0.05% were considered as candidates. Additionally, we checked each candidate for its silicagel/hexane elution order⁵⁾. Finally each peak was visually inspected for its shape and width. Only those, meeting all three criteria were used for quantitation.

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Exceptions were made for 4 compounds, marked with * (Table 1), due to their environmental importance. In these cases, either peak was broader, or RRT deviation was higher than 0.05% (but less than 0.1%), or elution order on silicagel/hexane column is not well-established yet. Amount of each identified congener in 1.00g of Camphechlor, and its percentage in Toxaphene (calculation based on 61.8% content of Toxaphene in Camphechlor) are given in Table 1.

Table 1. Concentrations of identified Toxaphene congeners in Camphechlor.

#	Chemical name, synonyms, Parlar # (where available)	Fractions	Amount (mg)	% (pure Toxaphene)
1	2-exo,3,3,5-exo,,6-endo,9,9,10,10-NCB	0	1.09	0.18
2	2,2,3-exo,5,5,9,9,10,10-NCB	0	1.80	0.29
3	2,2,3-exo,5,5,8,9,10,10-NCB, ToxC, #58	1,2	10.78	1.74
4	2,2,3-exo,5-endo,6-exo,8,9,9,10,10-DCB	1	1.76	0.28
5	2-exo,3,3,6,6,8,8,9,10,10-DCB, #69	1,2	0.85	0.14
6	2-exo,5,5,9,9,10,10-HpCB	2,3	0.24	0.04
7*	2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB, #26	2,3	2.48	0.40
8	2,2,5,5,9,9,10,10-OCB, #38	3,4	2.12	0.34
9*	2,2,3-exo,5-endo,6-exo,8,9,10,10-NCB and 2-exo,3,3,5-exo,6-endo,8,9,10,10-NCB	3,4	8.57	1.39
10	2-exo,3-endo,5-exo,9,9,10,10-HpCB, Tox7	4	0.42	0.07
11	2,2,5-endo,6-exo,8,8,9,10,10-NCB, #56	4	2.33	0.38
12	2,2,3-exo,5,5,8,9,9,10,10-DCB	4,5,6	1.51	0.24
13	2,2,5-endo,6-exo,8,9,9,10,10-NCB, #59	5,6	4.50	0.73
14	2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB,ToxA, #50	5,6,7	0.62	1.01
15	2,2,5,5,8,9,9,10,10-NCB, #62	6,7	1.09	1.76
16	2,2,3-exo,5-endo,6-exo,8,9,10-OCB, #39	7,8	3.10	0.50
17	2-exo,5,5,8,9,9,10,10-OCB, #44	7,8	2.22	0.36
18	2,2,5-endo,6-exo,8,8,9,10-OCB + 2,2,5-endo,6-exo,8,9,9,10-OCB, ToxA, #42a,b	9,10	13.7	2.22
19	2,2,5-endo,6-exo,8,9,10,10-OCB	9,10,11	5.02	0.81
20	2,2,5,5,8,9,10,10-OCB, #51	10,11	9.35	1.51
21	2-endo,3-exo,5-endo,6-exo,8,9,10,10-OCB, #40 + 2-exo,3-endo,5-exo,8,9,9,10,10-OCB, #41	11,12	7.27	1.18
22*	2-endo,3-exo,5-endo,6-exo,8,9,10-HpCB, Hp-Sed	12,13	2.40	0.39
23	2,2,5,5,6-exo,8,9,10-OCB	13	2.50	0.40
24*	2-exo,3-endo,6-exo,8,9,10-HxCB, Hx-Sed	13,14	0.96	0.16
	TOTAL		86.68	14.03

These numbers, as we realize, require further confirmation by MS and NMR, but certain careful conclusions can be made :

- there is no single congener with content >2%
- among identified congeners, only 7 or 8 (depending on the ratio of Parl #42a and #42b) represent >1% of Toxaphene

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- The famous BgVV3 - #26, 50 and 62 total to 3.17%(possibly less, for uncertainty with #26)
- “The Forties” - #40, 41, 42a,b and 44 total to 3.76%
- “The B Family” – Toxicant B and its chlorinated derivatives total to about 7%(content of B is around 1%, though we are not able yet to provide exact value due to co-eluters on GC)
- Content of Hx-Sed and Hp-Sed is 0.16% and 0.4%, respectively
- Content of 2-exo,3-endo,5-exo,9,9,10,10-HpCB is only 0.07%. This compound⁶⁾ was found in some biota samples in concentrations, similar to those of Parlar #26 or #50(0.4% and 1.01% respectively)

2. Weight distribution of Toxaphene congeners.

Analysis of each fraction is summarized in Table 2. The data for each fraction includes number of peaks, representing congeners in different quantities (>5mg, 1-5mg, 0.5-1mg, 0.1-0.5mg and total). The total quantity(in mg) is given for each group in each fraction and altogether.

Number of peaks is not equal to number of congeners, as congeners may elute in 2 or 3 fractions.

Table 2. Composition of fractions.

Fraction (volume)	Total quantity, >5mg (# of peaks)	Total quantity, 1-5mg (# of peaks)	Total quantity, 0.5-1mg(# of peaks)	Total quantity, 0.1-0.5mg (# of peaks)	Grand Total	Total % in Toxaphene
0(200ml)	0	2.89(2)	0.56(1)	0.82(4)	4.27(7)	0.69
1(40ml)	0	1.76(1)	0.92(1)	2.62(10)	5.30(12)	0.86
2(40ml)	9.86(1)	4.51(3)	2.59(4)	2.17(10)	19.13(18)	3.10
3(40ml)	6.14(1)	2.96(2)	1.80(3)	1.92(11)	12.82(17)	2.07
4(40ml)	0	7.76(4)	2.68(4)	2.42(9)	12.86(17)	2.08
5(40ml)	0	15.25(7)	2.79(4)	3.21(14)	21.25(25)	3.46
6(40ml)	12.64(2)	5.50(2)	4.03(6)	2.44(9)	24.61(19)	3.98
7(40ml)	0	15.46(9)	0	7.75(4)	23.21(13)	3.76
8(40ml)	0	2.84(2)	3.82(5)	2.57(2)	9.23(9)	1.49
9(60ml)	9.05(1)	7.70(4)	4.57(7)	3.90(11)	25.22(23)	4.08
10(60ml)	15.80(3)	4.22(3)	2.70(4)	2.96(12)	25.68(22)	4.16
11(60ml)	6.51(1)	7.27(4)	3.92(6)	2.67(13)	20.37(24)	3.30
12(60ml)	0	8.86(5)	5.04(7)	2.39(11)	16.29(23)	2.64
13(110ml)	0	16.53(6)	2.57(4)	2.58(8)	21.68(18)	3.51
14(130ml)	13.04(2)	4.88(2)	2.29(3)	5.07(20)	25.28(27)	4.09
15(200ml)	9.66(1)	4.05(2)	1.92(3)	3.55(16)	19.18(22)	3.10
16(250ml)	0	3.51(1)	1.61(2)	2.57(15)	7.69(18)	1.24
17(500ml)	0	3.26(2)	0	3.87(12)	7.13(14)	1.15
18(520ml)	0	3.50(1)	1.20(2)	2.92(18)	7.62(21)	1.23
19(160ml)	0	0	0	0.66(3)	0.66(3)	0.11
Total 0-19 (2.63L)	82.70 (12)	122.71 (62)	45.01 (66)	59.06 (212)	309.48 (352)	
% in Toxaphene	13.38	19.86	7.28	9.56	50.07	

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- 12 largest peaks (each >5mg) represent >13% of Toxaphene.
- 62 major peaks (each 1-5mg) represent almost 20%.
- 66 important peaks (each 0.5-1.0mg) represent another 7%.
- 212 smaller peaks (each 0.1-0.5) represent about 10%
- Together 352 peaks (roughly 176 congeners) represent 50% of Toxaphene
- Remaining 50% consist of thousands of minor compounds
- 1% content in Toxaphene corresponds to about 10 thousands tons, released into environment, and 0.01% - to 100 tons.

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