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EMERGENCE TEMPERATURE INDICES AND RELATIVE RETENTION TIMES OF PESTICIDES AND INDUSTRIAL CHEMICALS DETERMINED BY LINEAR PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

WILBUR L. SAXTON

U.S. Food and Drug Administration, 5009 Federal Office Building, Seattle, WA 98174 (U.S.A.)

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SUMMARY

Emergence temperature indices and relative retention times of nearly 600 pesticides and industrial chemicals are sequentially tabulated to provide a basis for the identification of unknowns detected on methyl silicone columns when programmed temperature gas chromatography is used. A technique of normalizing column parameters is described to enable duplication of the tabulated data on columns which have different dimensions, amount of stationary phase, and/or other operating parameters.

Suggestions for enhancing the precision with which these data can be reproduced on other equipment are presented.

INTRODUCTION

The initial identification of suitably volatile unknowns is frequently established by comparing the gas chromatographic retention measurement of the unknown with tabulated values obtained under nearly identical conditions. The retention measurements generally used for this purpose include Kovats Indices[1], other retention indices[2], relative retention times[3] and absolute retention times. Saxton recently demonstrated that emergence temperatures can also provide an index of chromatographic retention when linear, temperature programmed gas chromatography (PTGC) is used for the determinations[4]. This latter technique has the advantage of using one of the most significant gas chromatographic parameters as the retention measurement[5]. This parameter, the emergence temperature, is one that should be measured[5] and closely duplicated regardless of which type of retention measurement listed above is used for identification purposes.

The confidence with which an identification can be made by any of the methods depends on the precision with which the tabulated values can be duplicated during the analysis of the unknown. In order to assure precision of the retention measurements, the column parameters used to generate the tabulated data are traditionally reproduced as closely as possible. However, such a restrictive approach is unnecessary. It has recently been shown[6,7] that such retention data can be precisely duplicated even though the column parameters differ widely, as long as some parameters

are adjusted to compensate for the changes in others. Details of this method are discussed in this paper along with various approaches for obtaining good precision.

EXPERIMENTAL

Apparatus and reagents

   Gas chromatography. The gas chromatograph was a Hewlett-Packard 5830, equipped with a flame ionization detector. Operating conditions: injector, 150°C; detector, 350°C; nitrogen carrier gas, 30 ml/min. Column: borosilicate glass, 110 cm × 2 mm I.D., packed with 5% OV-101 on Chromosorb W HP (80–100 mesh). Column temperatures: initial temperature 50°C, immediately programmed linearly at 8.5°C/min to 300°C. The temperature program rate and carrier flow-rate were periodically adjusted to maintain an emergence temperature of 194 ± 1°C for chlorpyrifos.

   A Hamilton 10-μl syringe with a 4-in. needle was used.

   Standards. Most compounds were analytical reference standards obtained from the U.S. Environmental Protection Agency and were dissolved in isooctane at 1 μg/μl. Those compounds insoluble in isooctane were dissolved in methanol at the same concentration.

Procedure

   Samples were injected with a long syringe so they could be deposited into the void at the head of the column within the column oven to avoid possible thermal degradation. Approximately 1/2 μl of each of 1–8 compounds, along with chlorpyrifos as an internal reference compound, were injected per chromatographic run. The retention time differences between chlorpyrifos and each of the coinjected compounds were determined, and the emergence temperature index of each calculated by the equation

$$T_{e1} = T_{e2} + r(t_{R2} - t_{R1}) \tag{1}$$

where T_{e1} is the emergence temperature index of the compound of interest, T_{e2} is the tabulated emergence temperature index of a designated reference compound, r is the temperature program rate, and $(t_{R2} - t_{R1})$ is the difference in retention time between the compound of interest and the designated reference compound. A temperature of 193.8°C was substituted for T_{e2} in eqn. 1 when chlorpyrifos was used as the reference. If a compound was not separated from chlorpyrifos, phosalone was used as the internal reference compound and 237.9°C was substituted for T_{e2}.

   Relative retention times were calculated by the equation

$$r_{1/2} = t'_{R1}/t'_{R2} \tag{2}$$

where $r_{1/2}$ is the relative retention time (relative to chlorpyrifos) of the compound of interest, t'_{R1} is the adjusted retention time of the compound of interest and t'_{R2} is the adjusted retention time of chlorpyrifos. The adjusted retention time is the total retention time minus the retention time of an unretained substance.

DISCUSSION

In order to facilitate this discussion it is necessary to differentiate between the emergence temperature index that can be used for compound identification and the emergence temperature that is indicated by the oven temperature readout. The emergence temperature index is determined by measuring the temperature difference between the compound of interest and a reference compound which has been assigned a specific emergence temperature index value. For example, the emergence temperature index values tabulated for this report are based on the use of $n\text{-}C_{20}$ as the primary reference compound and 200.0°C as its emergence temperature index. Chlorpyrifos was used as the secondary reference compound because it can be detected by the element selective detectors frequently used for the determination of pesticides and industrial chemicals. The emergence temperature index of chlorpyrifos was calculated by using eqn. 1 and substituting 200.0°C, the emergence temperature index of $n\text{-}C_{20}$, for T_{e2}. The retention time difference between chlorpyrifos and $n\text{-}C_{20}$ was substituted for $t_{R2} - t_{R1}$. This resulted in an emergence temperature index of 193.8°C for chlorpyrifos.

The emergence temperature index of a compound can be much more precisely duplicated on various gas chromatographs than can emergence temperatures that are determined by the oven temperature readout or by multiplying the retention time by the temperature ramp rate and adding the initial temperature. Since they can be precisely determined, the emergence temperature indices of many pesticides and industrial chemicals are presented in Table I to provide a basis for the identification of unknowns detected while screening on methyl silicone columns by PTGC. Although relative retention times cannot usually be as precisely determined[6], they are included in Table I because they are familiar to many analysts.

The following subtopics discuss techniques which provide flexibility in the choice of column parameters and which enhance the precision with which data in Table I can be duplicated.

Use of simultaneous parameter compensation

Fig. 1 indicates the direction some parameters must be changed in order to compensate for changes in others if the emergence temperature of a designated compound is to be maintained. For example, if the column length were increased, either a faster flow-rate or slower temperature program rate could be used to compensate. It has been shown that if the column parameters are "normalized" in this manner to maintain the emergence temperature of one compound, then the emergence temperatures of all compounds are closely maintained as well[4]. The operating conditions of the column described in the experimental section were normalized so $n\text{-}C_{20}$ emerged and was detected just as the column reached 200 ± 1°C. Table II lists the chromatographic parameters of several typical methyl silicone columns which have been so normalized. Both Fig. 1 and Table II may serve as guides for selecting column parameters so as to duplicate the data in Table I. Equivalent results will be obtained if the column parameters are normalized so chlorpyrifos emerges at 194 ± 1°C.

Standardization of column temperatures

Emergence temperature indices and relative retention times can be precisely

TABLE I

RETENTION MEASUREMENTS OF COMPOUNDS* ANALYZED ON METHYL SILICONE COLUMNS NORMALIZED BY SIMULTANEOUS PARAMETER COMPENSATION SO n-EICOSANE EMERGES AT 200 ± 1°C (OR SO CHLORPYRIFOS EMERGES AT 194 ± 1°C)

T_e is the emergence temperature index, $r_{1/2}$ is the adjusted retention time relative to chlorpyrifos, T_t is the threshold temperature (the temperature at which the cold trapped compound begins moving through the column), and (a) indicates that additional peaks are listed for the compound. Some of the data are entered with fewer significant figures than most to indicate that those values are difficult to precisely duplicate, either because the compounds were not initially cold trapped or because they tailed excessively.

T_e	$r_{1/2}$	Formula	Compound
61	0.07	C_2Cl_4	Tetrachloroethylene
79	0.18	$C_4H_8Cl_2O$	Bis(2-chloroethyl) ether
80	0.20	C_6H_5ClO	o-Chlorophenol
81	0.21	CH_3ClHg	Methyl mercuric chloride
81	0.21	C_6H_6O	Phenol
83	0.21	$C_6H_4Cl_2$	p-Dichlorobenzene
83	0.23	$C_{10}H_{22}$	n-Decane (T_t = < 30°C)
85	0.24	$C_6H_4Cl_2$	o-Dichlorobenzene
88	0.26	$(C_2H_4O)n$	Metaldehyde
89	0.26	$C_3H_5Br_2Cl$	Dibromochloropropane
90	0.27	$C_{14}H_{18}N_4O_3$	Benomyl
91	0.28	$C_6H_5NO_2$	Nitrobenzene
91	0.28	C_2Cl_6	Hexachloroethane
92	0.29	$C_{15}H_{13}NO_3$	Duraset 20w (a)
95	0.31	$C_8H_{10}O$	2,4-Dimethylphenol
97	0.32	$C_9H_{14}O$	Isophorone
98	0.32	$C_6H_3Cl_3$	1,3,5-Trichlorobenzene
100.9	0.347	$C_5H_{10}Cl_2O_2$	Bis(2-chloroethoxy)methane
101	0.35	$C_8H_{20}O_7P_2$	TEPP
102.0	0.347	$C_{12}H_{26}O_6P_2S_4$	Dioxathion (a)
103	0.35	$C_6H_5NO_3$	2-Nitrophenol
103.0	0.350	$C_6H_3Cl_3$	1,2,4-Trichlorobenzene
104.0	0.367	$C_{10}H_8$	Naphthalene
107.3	0.382	$C_6H_3Cl_3$	1,2,3-Trichlorobenzene
109	0.40	$C_6H_4Cl_2O$	2,4-Dichlorophenol
109.8	0.410	C_4Cl_6	Hexachloro-1,3-butadiene
111.2	0.411	$C_{10}H_{12}ClNO_2$	Carbanolate (a)
117	0.45	$C_4H_7Cl_2O_4P$	Dichlorvos
117.2	0.452	$C_8H_{12}ClNO$	Allidochlor
120	0.47	$C_{15}H_{13}NO_3$	Duraset 20w (a)
121	0.48	C_7H_7ClO	4.Chloro-3-methylphenol
122.3	0.497	$C_7H_3Cl_2N$	Dichlobenil
122.8	0.502	$C_6H_2Cl_4$	1,2,3,5-Tetrachlorobenzene
122.8	0.502	$C_6H_2Cl_4$	1,2,4,5-Tetrachlorobenzene
124.9	0.515	C_5H_6	Hexachlorocyclopentadiene
125.7	0.520	$C_{10}H_{14}N_2$	Nicotine (a)
127.6	0.533	$C_9H_{19}NOS$	EPTC (T_t = 60°C)
128.2	0.542	$C_6H_2Cl_4$	1,2,3,4-Tetrachlorobenzene
128.6	0.543	$C_{10}H_xCl_y$	Halowax HX-1031
128.8	0.545	$C_{12}H_{10}$	Biphenyl
129.6	0.547	$C_{10}H_7Cl$	β-Chloronaphthalene
133	0.57	$C_6H_3Cl_3O$	2,4,6-Trichlorophenol
134	0.58	$C_2H_8NO_2PS$	Methamidophos

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
134.0	0.580	$C_6H_5Cl_2N$	3,4-Dichloroaniline
134.4	0.582	$C_7H_6Cl_2O_2$	Hydroxy chloroneb
135.6	0.589	$C_{12}H_{14}N_2O_5$	Dinex (a)
136	0.59	$C_7H_6N_2O_4$	2,6-Dinitrotoluene
136.9	0.601	$C_{12}H_8$	Acenapthylene (T_t = 85°C)
137.2	0.602	$C_{10}H_{10}O_4$	Dimethyl phthalate
138.1	0.608	$C_5H_5Cl_3N_2OS$	Etridiazole
138.5	0.611	$C_{10}H_{21}NOS$	Vernolate
138.7	0.611	$C_{12}H_{14}N_2O_5$	Dinex (a)
139	0.61	$C_7H_{13}O_6P$	Mevinphos
139.5	0.615	$C_{10}H_{13}NO_2$	Propham
140.0	0.616	$C_4H_8Cl_3O_4P$	Trichlorfon
141	0.62	$C_8H_9NO_2$	*cis*-4-Cyclohexene-1,2-dicarboximide
141.4	0.631	$C_7H_2Cl_6$	Hexachloronorbornadiene
141.7	0.631	$C_{12}H_{10}$	Acenapthene
141.8	0.644	$C_{10}H_{14}N_2$	Nicotine (a)
142	0.64	$C_{12}H_{15}NO_4$	3-Hydroxycarbofuran
144	0.65	$C_{10}H_8O$	α-Napthol
144.1	0.651	$C_8H_8Cl_2O_2$	Chloroneb
144.4	0.652	$C_{12}H_{10}O$	*o*-Phenylphenol
145	0.65	$C_9H_{11}Cl_3NO_4P$	Chlorpyrifos oxygen analogue
145	0.65	$C_6H_4N_2O_5$	2,4-Dinitrophenol
146	0.66	$C_7H_6N_2O_4$	2,4-Dinitrotoluene
146.0	0.664	C_6HCl_5	Pentachlorobenzene
146.3	0.666	$C_9H_{17}NOS$	Molinate
146.4	0.667	$C_6Cl_4O_2$	Chloranil
147.1	0.677	$C_8H_5Cl_3O_2$	Methyl 2,3,6-Trichlorobenzoate
149	0.68	$C_4H_{10}NO_3PS$	Acephate
149.8	0.690	$C_{12}H_{21}N_2O_4P$	Diazinon oxygen analogue
150.9	0.694	$C_{10}H_{13}ClO_2$	MCPA, methyl ether
152.5	0.710	$C_7H_2Cl_6O$	Epoxyhexachloronor-borene
152.7	0.710	$C_8H_{19}O_4PS$	Demeton-*o*, oxygen analogue
152.7	0.712	$C_{13}H_{10}$	Fluorene
153	0.71	$C_7H_{13}N_3O_3S$	Oxamyl (a)
153.4	0.717	$C_6HCl_4NO_2$	Tecnazene
153.6	0.718	$C_{12}H_{14}O_4$	Diethyl phthalate
153.8	0.719	$C_7H_6N_2O_5$	DNOC
154	0.72	$C_7H_6N_2O_5$	2-Methyl-4,6-dinitrophenol
154	0.72	$C_{13}H_{24}N_3O_4P$	Pirimiphos ethyl oxygen analogue
154	0.72	$C_6H_5NO_3$	4-Nitrophenol
155	0.72	$C_7H_{11}N_3O_2$	Metribuzin, deaminated diketo metabolite
155	0.72	$C_{19}H_{23}N_3$	Amitraz
155.1	0.724	$C_8H_{13}N_2O_3PS$	Thionazin
155.4	0.730	$C_{11}H_{14}ClNO$	Propachlor
155.9	0.733	$C_{11}H_{15}NO3$	Propoxur
156	0.74	$C_6H_{12}N_2O_3$	Daminozide
156.2	0.735	$C_{12}H_{11}N$	Diphenylamine
156.4	0.738	$C_8H_{19}O_3PS_2$	Demeton-*o*
156.7	0.739	$C_7H_{17}O_3PS_2$	Phorate oxygen analogue
156.7	0.739	$C_6H_{15}O_3PS_2$	Metasystox thiol
157	0.74	$C_5H_{12}NO_4PS$	Omethoate
157	0.74	$C_7H_{13}N_3O_3S$	Oxamyl (a)

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
157.8	0.747	$C_7H_3Cl_7$	Heptachloronorbornene
157.9	0.749	$C_6H_{15}O_3PS_2$	Methyl demeton
158	0.75	$C_{12}H_{12}N_2$	1,2-Diphenylhydrazine (a)
158.0	0.749	$C_6H_{15}O_3PS_2$	Metasystox thiono
158.3	0.750	$C_9H_8Cl_2O_3$	2,4-D methyl ester
158.8	0.755	$C_{11}H_{21}NOS$	Cycloate
159	0.76	$C_{12}H_{10}N_2O$	N-Nitrosodiphenylamine
159.2	0.757	$C_9H_{12}N_2O$	Fenuron
159.2	0.757	$C_8H_{16}NO_5P$	Ethoprop
159.6	0.759	$C_{16}H_{34}$	*n*-Hexadecane (T_i = 105°C)
160.6	0.762	$C_8H_9O_3PS$	Salithion
160.6	0.765	$C_4H_7Br_2Cl_2O_4P$	Naled
160.8	0.765	$C_{10}H_{13}ClN_2$	Chlordimeform
161	0.77	$C_{10}H_{11}F_3N_2O$	Fluometuron
161	0.77	$C_7H_3Br_2NO$	Bromoxynil
161	0.77	$C_{10}H_{14}Cl_2N_2$	Chlordimeform hydrochloride
161.1	0.770	$C_{10}H_{12}ClNO_2$	Chlorpropham
161.3	0.771	$C_{14}H_{18}O_4$	Diisopropyl phthalate
161.5	0.777	$C_7H_5Cl_2NO$	2,6-Dichlorobenzamide
162.1	0.779	$C_{11}H_{13}NO_4$	Bendiocarb
163	0.78	$C_{16}H_{16}N_2O_4$	Phenmedipham
163.0	0.783	$C_6H_6Cl_6$	α-BHC
163.2	0.783	$C_8H_6Cl_2O_3$	Dicamba
164.0	0.786	$C_8H_{14}ClNS_2$	Sulfallate
164.2	0.791	$C_8H_{20}O_5P_2S_2$	Sulfotep
164.5	0.794	$C_{12}H_9BrO$	4-Bromo-diphenyl ether
164.6	0.795	$C_7H_{17}O_2PS_3$	Phorate
164.6	0.791	$C_{13}H_{12}O_2$	1-Napthalene acetic acid methyl ester
164.8	0.796	$C_{10}H_{14}N_2$	Nicotine (a)
165	0.80	$C_8H_{16}NO_5P$	Dicrotophos
165.0	0.799	$C_{13}H_{19}NO_2$	Bufencarb (a)
165.5	0.801	$C_{10}H_{15}O_2PS$	Fonofos oxygen analogue
165.6	0.802	$C_6H_4Cl_2N_2O_2$	Dicloran
165.6	0.802	$C_{10}H_{17}Cl_2NOS$	Diallate (a)
165.6	0.802	$C_{11}H_{12}Cl_2O_3$	2,4-D isopropyl ester (a)
165.7	0.803	$C_6H_6Cl_6$	β-BHC
165.9	0.803	$C_6H_{15}O_2PS_3$	Thiometon
166	0.80	$C_{10}H_{11}ClO_3$	Mecoprop
166	0.80	$C_7H_{12}N_4O_2$	Metribuzin, diketo metabolite
166.1	0.806	$C_{13}H_{16}F_3N_3O_4$	Trifluralin
166.4	0.808	$C_{13}H_{16}F_3N_3O_4$	Benfluralin
166.6	0.809	$C_{10}H_{17}Cl_2NOS$	Diallate (a)
166.6	0.809	C_6Cl_6	Hexachlorobenzene
167	0.81	$C_7H_{14}NO_5P$	Monocrotophos
167.7	0.817	$C_7H_3Cl_5O$	Pentachlorophenyl-methyl ether
168	0.82	$C_5H_{12}NO_3PS_2$	Dimethoate
168.3	0.818	$C_{11}H_{12}Cl_2O_3$	2,4-D isopropyl ester (a)
168.5	0.820	$C_8H_{19}O_3PS_2$	Demeton-S
168.6	0.820	$C_{11}H_{15}NO_2$	Trimethacarb
168.8	0.824	$C_{12}H_{15}NO_3$	Carbofuran
169.2	0.827	$C_6H_6Cl_6$	Lindane (T_i = 90°C)
169.6	0.830	$C_{14}H_{19}NO$	Ethoxyquin

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
169.9	0.830	$C_{10}H_{12}ClNO_2$	Carbanolate (a)
170	0.83	$C_{16}H_{16}N_2O_4$	Desmedipham
170.3	0.834	$C_8H_7Cl_2NO_2$	Chloramben methyl ester
170.3	0.835	$C_8H_{14}ClN_5$	Atrazine
170.5	0.836	$C_6H_6Cl_6$	γ-BHC
170.8	0.836	$C_{10}H_{19}N_5O$	Prometon
171	0.84	$C_7H_{12}ClN_5$	Simazine
171.1	0.840	C_6HCl_5O	Pentachlorophenol
171.3	0.841	C_7Cl_5N	Pentachlorobenzonitrile
171.4	0.841	$C_{13}H_{19}NO_2$	Bufencarb (a)
171.4	0.842	$C_6Cl_5NO_2$	Quintozene
171.7	0.843	$C_9H_{10}NOPS$	Cyanophos
171.9	0.844	$C_9H_{16}ClN_5$	Propazine
171.9	0.844	$C_{10}H_9Cl_3O_3$	Silvex methyl ester
172	0.85	$C_7H_3Cl_3O_2$	2,3,6-TBA
172	0.85	$C_3H_6N_2S$	Ethylene thiourea
172.8	0.852	$C_{14}H_{10}$	Phenanthrene
173.1	0.853	$C_{10}H_4Cl_2O_2$	Dichlone
173.2	0.856	$C_{10}H_{15}OPS_2$	Fonofos
173.3	0.857	C_2I_4	Tetraiodoethylene
173.6	0.858	$C_{13}H_{19}NO_2$	Bufencarb (a)
173.7	0.869	$C_8Cl_4N_2$	Chlorothalonil
173.8	0.860	$C_{14}H_{10}$	Anthracene
173.8	0.860	$C_9H_{21}O_2PS_3$	Terbufos
174.0	0.861	$C_9H_7Cl_3O_3$	2,4,5-T methyl ester
175.2	0.869	$C_{12}H_{11}Cl_2NO$	Pronamide
175.3	0.870	$C_{10}H_6Cl_6$	Chlordene
175.4	0.870	$C_{14}H_{14}O_3$	Pival
175.5	0.871	$C_8H_{10}NO_6P$	Parathion-methyl oxygen analogue
176.4	0.876	$C_8H_{19}O_2PS_3$	Disulfoton
176.8	0.880	$C_{14}H_{16}F_3N_3O_4$	Profluralin
176.8	0.881	$C_{10}H_{12}N_2O_6$	Dinoseb
177	0.88	$C_{12}H_{10}O_2$	Naphthaleneacetic acid
177.1	0.882	$C_9H_9Cl_2NO_2$	2,3-Sirmate
177.1	0.882	$C_{12}H_{21}N_2O_3PS$	Diazinon ($T_1 = 100°C$)
177.2	0.883	$C_8H_3Cl_5O_2$	Pentachlorophenol acetate
177.3	0.884	$C_9H_9Cl_2NO_2$	Dichlormate
177.4	0.884	$C_{12}H_{12}N_2$	1,2-Diphenylhydrazine (a)
177.4	0.885	$C_9H_{13}ClN_2O_2$	Terbacil
177.6	0.885	$C_{10}H_{11}ClN_2$	BH 584
177.8	0.887	$C_8H_{10}N_4O_2$	Caffeine
178.0	0.898	$C_{13}H_{19}NO_2$	Bufencarb (a)
178.1	0.890	$C_{12}H_{13}ClF_3N_3O_4$	Fluchloralin
178.4	0.892	$C_{12}H_{18}N_2O_2$	Mexacarbate
179.1	0.896	$C_{10}H_{16}Cl_3NOS$	Triallate
179.2	0.898	$C_7H_5Cl_2NS$	Chlorthiamid
179.2	0.898	$C_6H_2Cl_5N$	Pentachloroaniline
179.9	0.900	$C_8H_{24}N_4O_3P_2$	Schradan
180.0	0.903	$C_9H_{11}BrN_2O_2$	Metrobromuron
180.2	0.903	$C_{12}H_{14}Cl_2O_3$	2,4-D isobutyl ester
180.4	0.907	$C_{10}H_{19}ClNO_5P$	Phosphamidon (a)
180.9	0.908	$C_{11}H_{12}Cl_2O_3$	4-(2,4-DB-) methyl ester

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
180.9	0.908	$C_{11}H_{18}N_4O_2$	Pirimicarb
181.5	0.913	$C_8H_{16}N_4OS$	Metribuzin
181.8	0.915	$C_8H_8Cl_3O_4P$	Ronnel oxygen analogue
182	0.91	$C_8H_{13}N_3OS$	Metribuzin, deaminated metabolite
182.0	0.916	$C_{10}H_6Cl_6$	Compound C
182.6	0.921	$C_7H_{17}O_5PS_2$	Phorate oxygen analogue sulfone
182.6	0.921	$C_{11}H_{11}Cl_3O_3$	2,4,5-T isopropyl ester
182.8	0.922	$C_{16}H_{22}O_4$	Diisobutyl phthalate
183.1	0.923	$C_9H_9Cl_2NO$	Propanil
183.1	0.925	$C_8H_{10}NO_5PS$	Parathion-methyl
183.3	0.926	$C_{10}H_{13}Cl_2O_3PS$	Dichlofenthion
184.3	0.933	$C_{12}H_{14}Cl_2O_3$	2,4-D *n*-butyl ester
184	0.93	$C_{12}H_{15}NO_4$	3-Hydroxycarbofuran (a)
184.4	0.934	$C_{12}H_{11}NO_2$	Carbaryl
184.6	0.936	$C_8H_{15}N_5S$	Simetryn
184.6	0.936	$C_{10}H_9NO_2S$	Mobam
184.7	0.936	$C_{12}H_9Cl_2NO_3$	Vinclozolin
184.9	0.937	$C_{10}H_{19}ClNO_5P$	Phosphamidon (a)
185	0.94	$C_{11}H_{13}ClO_3$	MCPB
185.3	0.939	$C_{10}H_9Cl_2NO$	Dicryl
185.7	0.943	$C_6H_{15}O_5PS_2$	Oxydemeton-methyl sulfone
185.8	0.945	$C_{10}H_{19}O_7PS$	Malathion oxygen analogue
185.9	0.945	$C_{10}H_5Cl_7$	Heptachlor
186.2	0.947	$C_9H_{17}N_5S$	Ametryn
186.3	0.948	$C_{14}H_{20}ClNO_2$	Alachlor
186.6	0.949	$C_{10}H_6Cl_6$	α-Chlordene
186.9	0.951	$C_6H_3Cl_3N_2O_2$	Picloram
187	0.95	$C_6H_{15}O_4PS_2$	Oxydemeton-methyl
187.0	0.953	$C_{10}H_{14}NO_6P$	Parathion oxygen analogue
187.1	0.953	$C_{10}H_{19}N_5S$	Prometryn
187.2	0.953	$C_{14}H_{12}Cl_2O$	Chlorfenthol (a)
187.3	0.954	$C_8H_8Cl_3O_3PS$	Ronnel
187.4	0.955	$C_{13}H_8Cl_2O$	*o,p'*-Dichlorobenzophenone
187.4	0.955	$C_{14}H_{12}Cl_2O$	Chlorfenthol (a)
187.5	0.956	$C_{15}H_{21}NO_4$	Metalaxyl
188	0.96	$C_{10}H_{16}NO_3PS$	Aminoparathion (a)
188.4	0.962	$C_{14}H_9Cl_5O$	*o,p*-Dicofol (a)
188.9	0.965	$C_9H_{12}NO_5PS$	Fenitrothion
189.4	0.969	$C_{10}H_{19}N_5S$	Terbutryn
189.5	0.970	$C_{12}H_{15}N_2O_4P$	Phoxim oxygen analogue
189.5	0.970	$C_{11}H_{15}NO_2S$	Methiocarb
189.7	0.972	$C_{15}H_{15}ClN_2O_2$	Chloroxuron
189.7	0.972	$C_7H_3Cl_5S$	Pentachlorophenyl methyl sulfide
189.9	0.972	$C_{16}H_{22}Cl_2O_3$	2,4-D ethyl hexyl ester (a)
190.0	0.973	$C_9H_{11}Cl_2FNO_2S_2$	Dichlofluanid
190.2	0.975	$C_{13}H_{18}O_5S$	Ethofumesate
190.2	0.975	$C_9H_{10}Cl_2N_2O_2$	Linuron
190.6	0.977	$C_9H_{13}BrN_2O_2$	Bromacil
190.8	0.979	$C_{13}H_{15}N_2O$	Norea
191.0	0.980	$C_{11}H_{20}N_3O_3PS$	Pirimiphos-methyl
191.0	0.980	$C_7H_{17}O_4PS_3$	Phorate sulfone
191.1	0.981	$C_7H_{17}O_3PS_3$	Phorate sulfoxide

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
191.3	0.982	$C_{10}H_{14}Cl_2NO_2PS$	Zytron
191.4	0.983	$C_{10}H_6Cl_6$	γ-Chlordene
191.8	0.986	$C_{16}H_{22}O_4$	Dibutyl phthalate
192.0	0.987	$C_{10}H_xCl_y$	Halowax 1000
192.2	0.989	$C_9H_{13}ClN_6$	Cyanazine
192.2	0.989	$C_{10}H_{19}O_6PS_2$	Malathion
192.3	0.991	$C_{10}H_6Cl_6$	β-Chlordene
192.6	0.992	$C_{12}H_8Cl_6$	Aldrin
192.8	0.993	$C_{10}H_{15}O_3PS_2$	Fenthion
192.9	0.994	$C_{10}H_6Cl_8$	Compound K (a)
193	0.99	$C_{14}H_9Cl_5O$	p,p'-Dicofol (a)
193.0	0.994	$C_{13}H_8Cl_2O$	p,p'-Dichlorobenzophenone
193.0	0.994	$C_{14}H_{12}Cl_2O$	Chlorfenthol (a)
193.3	0.996	$C_{10}H_6Cl_6O$	1-Hydroxychlordene
193.4	0.997	$C_{10}H_{14}NO_5PS$	Parathion
193.8	1.000	$C_9H_{11}Cl_3NO_3PS$	Chlorpyrifos ($T_i = 120°C$)
194.2	1.003	$C_{12}H_{13}Cl_3O_3$	2,4,5-T butyl ester (a)
194.4	1.004	$C_{15}H_{15}NO$	Desmethyl diphenamid
195	1.01	$C_{12}H_{26}O_6P_2S_4$	Dioxathion (a)
195.2	1.009	$C_{10}H_6Cl_4O_4$	DCPA
195.2	1.010	$C_9H_4Cl_8O$	Isobenzan
195.2	1.010	$C_{14}H_{16}ClN_3O_2$	Tridimefon
195.7	1.012	$C_8H_{19}O_3PS_2$	Demeton-S
196.0	1.017	$C_8H_{19}O_5PS_2$	Demeton-S sulfone
196.3	1.018	$C_{11}H_{11}Cl_3O_3$	4-(2,4,5-TB) methyl ester
196.4	1.018	$C_{16}H_{17}NO$	Diphenamid
196.6	1.020	$C_8H_8BrCl_2O_3PS$	Bromophos
196.8	1.021	$C_{12}H_8Cl_6$	Isodrin
197.4	1.025	$C_9H_8Cl_3NO_2S$	Captan
197.4	1.025	$C_{12}H_9NS$	Phenothiazine
197.4	1.026	$C_{10}H_9Cl_2NO$	Cypromid
197.7	1.028	$C_{12}H_{19}ClNO_3P$	Crufomate
198.0	1.030	$C_{12}H_{13}Cl_3O_3$	2,4,5-T butyl ester (a)
198.2	1.031	$C_{14}H_9Cl_3$	TDE, o,p-olefin
198.5	1.034	$C_{17}H_{25}NO_2$	MGK 264
199.0	1.036	$C_{10}H_5Cl_7O$	Heptachlor epoxide
199.0	1.037	$C_9H_5Cl_3N_4$	Anilazine
199.2	1.038	$C_{13}H_{24}N_3O_3PS$	Pirimiphos-ethyl
199.3	1.039	$C_{12}H_9ClO_2S$	Sulphenone
199.4	1.040	$C_{13}H_{19}N_3O_4$	Pendimethalin
199.5	1.040	$C_9H_4Cl_3O_2NS$	Folpet
199.6	1.040	$C_{10}H_7N_3S$	Thiabendazole
199.7	1.041	$C_{10}H_{13}ClFNOS$	Tolyfluanid
199.8	1.042	$C_{10}H_4Cl_8O$	Octachlor epoxide
200	1.05	$C_9H_{19}O_4PS_2$	Demeton-S-sulfoxide
200	1.05	$C_8H_{19}O_4PS_2$	Demeton-O-sulfoxide
200.0	1.045	$C_{20}H_{42}$	n-Eicosane ($T_i = 145°C$)
201	1.05	$C_{10}H_{16}NO_3PS$	Aminoparathion (a)
201	1.05	$C_{10}H_{14}Cl_6N_4O_2$	Triforine
201.3	1.053	$C_{12}H_{14}Cl_3O_4P$	α-Chlorfenvinphos
201.3	1.053	$C_{12}H_{14}Cl_3O_4P$	β-Chlorfenvinphos
201.3	1.053	$C_{12}H_{17}O_4PS_2$	Phenthoate

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
201.7	1.056	$C_{10}H_{20}NO_5PS_2$	Mecarbam
201.7	1.056	$C_{10}H_6N_2OS_2$	Oxythioquinox
201.8	1.057	$C_{15}H_{24}NO_4PS$	Isofenphos
201.8	1.057	$C_{13}H_{10}Cl_2S$	Chlorbenside
202	1.06	$C_{16}H_{10}$	Fluoranthene
202.0	1.058	$C_{12}H_{27}PS_3$	Merphos (a)
202.5	1.061	$C_6H_{11}N_2O_4PS_3$	Methidathion
202.6	1.061	$C_{13}H_{11}Cl_2NO_2$	Procymidione
203.1	1.065	$C_{10}H_6Cl_8$	*trans*-Chlordane
203.1	1.065	$C_{16}H_{10}$	Pyrene
203.9	1.071	$C_{14}H_{19}O_6P$	Crotoxyphos
204.0	1.072	$C_{19}H_{26}O_3$	Allethrin
204.1	1.073	$C_{14}H_9Cl_3$	*p,p'*-TDE olefin
204.2	1.074	$C_9H_6N_2S_3$	TCMTB
204.2	1.074	$C_8H_{19}O_4PS_3$	Disulfoton sulfone
204.4	1.075	$C_{10}H_{16}NO_5PS_2$	Famphur
204.8	1.078	$C_8H_{19}O_3PS_3$	Disulfoton sulfoxide
205	1.08	$C_{12}H_9Cl_2NO$	Amino-nitrofen
205.0	1.079	$C_{14}H_8Cl_4$	*o,p'*-DDE
205.1	1.081	$C_{12}H_8Cl_2O_3S$	Genite
205.2	1.081	$C_9H_6Cl_6O_3S$	Endosulfan I
205.3	1.082	$C_{10}H_{12}BrCl_2O_3PS$	Bromophos-ethyl
205.4	1.083	$C_{18}H_{19}Cl$	*p,p'*-Perthane olefin
206.0	1.086	$C_{10}H_9Cl_4O_4P$	Gardona
206.2	1.087	$C_9H_{12}ClO_3PS_2$	Methyl trithion oxygen analogue
206.2	1.089	$C_{12}H_8Cl_2O_3S$	Ovex
206.2	1.089	$C_{10}H_6Cl_8$	*cis*-Chlordane
207.0	1.093	$C_{18}H_{38}O$	1-Octadecanol (T_i = 150°C)
207.1	1.094	$C_{15}H_{12}Cl_2O_2$	DDA, *p,p'*-methyl ester
207.9	1.099	$C_{10}H_5Cl_9$	*trans*-Nonachlor
208.0	1.100	$C_{17}H_{21}NO_2$	Napropamide
208.3	1.104	$C_{13}H_{22}NO_3PS$	Fenamiphos
209.1	1.108	$C_{18}H_{26}O_4$	Dipentyl phthalate
209.7	1.112	$C_{11}H_{15}Cl_2PO_2S_2$	Prothiophos
209.7	1.113	$C_{16}H_{22}Cl_2O_3$	2,4-D ethylhexyl ester (a)
209.8	1.113	$C_{16}H_{22}Cl_2O_3$	2,4-D isooctyl ester (a)
209.8	1.113	$C_{12}H_{14}N_2O_5$	Dinex (a)
209.8	1.113	$C_{11}H_9Cl_2NO_2$	Barban
209.9	1.113	$C_{14}H_{15}Cl_2N_3O_4$	Imazalil
210.0	1.113	$C_{12}H_8Cl_6O$	Dieldrin
210.3	1.116	$C_{12}H_{13}NO_2S$	Carboxin
210.7	1.119	$C_{14}H_8Cl_4$	*p,p'*-DDE (T_i = 140°C)
211.2	1.123	$C_{12}H_{27}PS_3$	Merphos (a)
211.3	1.124	$C_{12}H_{28}O_4P_2S_4$	Phostex
211.3	1.124	$C_{14}H_{10}Cl_4$	*o,p'*-TDE
211.3	1.124	$C_{12}H_{27}OPS_3$	DEF
212.4	1.132	$C_{10}H_{12}ClN_3O_2$	Tranid
212.7	1.133	$C_{15}H_{18}Cl_2N_2O_3$	Oxadiazon
212.9	1.135	$C_{12}H_7Cl_2NO_3$	Nitrofen
213.1	1.135	$C_{12}H_8Cl_6O$	Endrin
213.2	1.137	$C_{15}H_{23}ClO_4S$	Aramite (a)
213.3	1.137	$C_{15}H_{11}ClF_3NO_4$	Oxyfluorfen

TABLE I *(continued)*

T_e	$r_{1/2}$	Formula	Compound
213.6	1.141	$C_{16}H_{22}Cl_2O_3$	2,4-D ethylhexyl ester (a)
213.6	1.141	$C_9H_6Cl_6O_3S$	Endosulfan II
213.8	1.143	$C_{16}H_{22}Cl_2O_3$	2.4-D isooctyl ester (a)
214.4	1.147	$C_9H_{12}ClO_2PS_3$	Methyl trithion
215.3	1.151	$C_{18}H_{20}Cl_2$	Perthane
215.8	1.156	$C_{15}H_{18}N_2O_6$	Binapacryl
216.3	1.160	$C_{12}H_8Cl_6O$	Endrin aldehyde
216.7	1.164	$C_9H_{18}FeN_3S_6$	Ferbam
216.7	1.164	$C_{15}H_{14}Cl_2NO_2$	Dilan (a)
216.8	1.164	$C_{16}H_{14}Cl_2O_3$	Chlorobenzilate
216.8	1.164	$C_6H_{12}N_2S_4$	Thiram
217.0	1.164	$C_{14}H_{10}Cl_4$	p,p'-TDE
217.1	1.165	$C_{13}H_{11}Cl_2O_2PS$	Leptophos photo product
217.2	1.166	$C_{15}H_{19}Cl_3O_4$	2,4,5-T PGB ether esters (a)
217.4	1.167	$C_{11}H_{13}Cl_2N_3O_4$	Chlornidine
217.6	1.168	$C_{22}H_{46}$	n-Docosane ($T_t = 160°C$)
217.8	1.169	$C_{10}H_5Cl_9$	cis-Nonachlor
218.4	1.173	$C_{11}H_{17}O_4PS_2$	Fensulfothion (a)
218.4	1.173	$C_{14}H_9Cl_5$	o,p'-DDT
218.7	1.174	$C_{10}H_6Cl_8$	Compound K (a)
218.9	1.175	$C_9H_{22}O_4P_2S_4$	Ethion
219.5	1.181	$C_8H_9ClNO_5PS$	Chlorthion
219.7	1.183	$C_{12}H_6Cl_4S$	Tetrasul
220.6	1.190	$C_{10}Cl_{10}O$	Chlordecone
220.6	1.190	$C_{12}H_{19}O_2PS_3$	Sulprofos
220.8	1.192	$C_{13}H_{19}N_3O_6S$	Nitralin
221.0	1.193	$C_9H_6Cl_6O_4S$	Endosulfan sulfate
221.2	1.195	$C_{15}H_{13}Cl_2NO_2$	Prolan
221.5	1.195	$C_{15}H_{14}Cl_2NO_2$	Dilan (a)
221.6	1.195	$C_{14}H_{18}N_4O_4S_2$	Thiophanate
221.6	1.195	$C_{11}H_{17}O_4PS_2$	Fensulfothion (a)
221.9	1.201	$C_{11}H_{16}ClO_2PS_3$	Carbophenothion
222.0	1.201	$C_{18}H_{24}O_6$	Butyl phthalyl butyl glycolate
222.0	1.201	$C_{11}H_{12}NO_5PS$	Phosmet oxygen analogue
222.4	1.202	$C_{12}H_9ClF_3N_3O$	Norflurazon
223.8	1.210	$C_{19}H_{20}O_4$	Butylbenzene phthalate
224.0	1.212	$C_{14}H_9Cl_5$	p,p'-DDT ($T_t = 150°C$)
224.4	1.214	$C_{10}H_9Cl_4NO_2S$	Captafol
224.5	1.215	$C_{16}H_{13}Cl_2N_3O_2$	Tilt
225.5	1.223	$C_8H_{12}NO_5PS_2$	Cythioate
226	1.23	$C_{10}H_8ClN_3O$	Pyrazon
226.1	1.227	$C_{16}H_{15}Cl_3O_2$	o,p'-Methoxychlor
226.2	1.228	$C_{16}H_{15}Cl_2NO_2$	Bulan
226.5	1.230	$C_{15}H_{14}Cl_2NO_2$	Dilan (a)
227.6	1.237	$C_{12}H_8Cl_6O$	Endrin ketone
227.7	1.239	$C_{16}H_{15}Cl_2O_4$	Diclofop-methyl
228.4	1.244	$C_{19}H_{26}O_4S$	Propargite
228.6	1.245	$C_8Br_4O_3$	Tetrabromo phthalic anhydride
228.9	1.250	$C_{10}H_{12}N_3O_4PS$	Azinphos methyl oxygen analogue
229.1	1.252	$C_{11}H_{16}ClO_5PS_2$	Carbophenothion oxygen analogue sulfone
229.1	1.252	$C_{12}H_9Cl_7O$	Dieldrin chlorohydrin
229.9	1.253	$C_{11}H_{12}O_4NPS_2$	Phosmet

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
230.2	1.260	$C_{19}H_{30}O_5$	Piperonyl butoxide
230.8	1.260	$C_{11}H_{16}ClO_4PS_2$	Carbophenothion oxygen analogue sulfoxide
230.9	1.260	C_6Br_6	Hexabromobenzene
231.2	1.263	$C_{13}H_{13}Cl_2N_3O_2$	Iprodione
231.3	1.264	$C_{20}H_{27}O_4P$	α-Ethylhexyl diphenyl phosphate
231.3	1.264	$C_{13}H_{22}NO_5PS$	Fenamiphos sulfone
231.6	1.265	$C_{11}H_{15}NO_3S$	Methiocarb sulfoxide
231.9	1.268	$C_{13}H_{10}BrCl_2O_3P$	Leptophos oxygen analogue
232	1.27	$C_{19}H_{22}O_6$	Gibberellic acid
232.4	1.274	$C_{14}H_{14}NO_4PS$	EPN
233	1.27	$C_{18}H_{12}$	Chrysene
233	1.28	$C_{12}H_{10}Cl_2N_2$	3,3'-Dichlorobenzidine
233.5	1.279	$C_{17}H_{16}Br_2O_3$	Bromopropylate
233.7	1.280	$C_{12}H_8Cl_6O$	Photodieldrin
233.8	1.281	$C_{24}H_{50}$	*n*-Tetracosane ($T_i = 180°C$)
233.8	1.281	$C_{14}H_9Cl_5O$	*p,p'*-Dicofol (a)
233.9	1.282	$C_{16}H_{15}Cl_3O_2$	*p,p'*-Methoxychlor
234.0	1.285	$C_{18}H_{12}$	1,2-Benzanthracene
234.1	1.285	$C_{14}H_2N_4O_6S$	Oryzalin-dimethyl
234.9	1.289	$C_{20}H_{30}O_6$	Dibutoxyethyl phthalate (a)
234.9	1.290	$C_{12}H_6Cl_4OS$	Tetrasul sulfoxide
235	1.29	$C_{13}H_{22}NO_3PS$	Fenamiphos
236.2	1.299	$C_{11}H_{16}ClO_4PS_3$	Carbophenothion sulfone
236.3	1.304	$C_{12}H_6Cl_4O_2S$	Tetradifon
236.5	1.307	$C_{10}H_{12}N_3O_3PS_2$	Azinphos-methyl
236.7	1.307	$C_{20}H_{26}O_4$	Dicylohexyl phthalate
237.6	1.308	$C_{20}H_{14}O_4$	Diphenyl phthalate
237.9	1.310	$C_{13}H_{13}Cl_2N_3O_2$	Iprodione metabolite isomer
237.9	1.311	$C_{12}H_{15}ClNO_4PS_2$	Phosalone
238.3	1.314	$C_{11}H_{16}ClO_3PS_3$	Carbophenothion sulfoxide
239.1	1.319	$C_{13}H_{10}BrCl_2O_2PS_2$	Leptophos
239.4	1.326	$C_{15}H_{19}Cl_3O_4$	2,4,5-T PGB ether esters (a)
240.5	1.333	$C_{10}Cl_{12}$	Mirex
241	1.33	$C_{14}H_4N_2O_2S_2$	Dithianon
241	1.33	$C_{18}H_{34}OSn$	Cyhexatin
241.0	1.332	$C_xH_yO_4$	Hatcol 149 (a)
241.4	1.334	$C_{24}H_{38}O_4$	Di-ethylhexyl phthalate
241.4	1.334	$C_{24}H_{38}O_4$	Di-isooctyl phthalate (a)
241.9	1.339	$C_{10}H_xCl_y$	Halowax 1051 (a)
242	1.34	$C_{10}H_{10}Cl_2O_3$	4-(2,4-D)B
242.4	1.341	$C_{17}H_{12}Cl_2N_2O$	Fenarimol
243.6	1.350	$C_{12}H_{16}N_3O_3PS_2$	Azinphos-ethyl
244.2	1.354	$C_{24}H_{38}O_4$	Di-isooctyl phthalate (a)
244.8	1.359	$C_{14}H_{17}ClNO_4PS_2$	Dialifor
246.1	1.374	$C_{14}H_{16}ClO_6P$	Coumaphos oxygen analogue
247.9	1.380	$C_{12}H_{18}N_4O_6S$	Oryzalin
248.0	1.381	$C_{24}H_{38}O_4$	Di-isooctyl phthalate (a)
248.6	1.389	$C_{26}H_{54}$	*n*-Hexacosane ($T_i = 195°C$)
250.2	1.396	$C_{21}H_{20}Cl_2O_3$	*cis*-Permethrin
250.6	1.400	$C_{14}H_{16}ClO_5PS$	Coumaphos
251	1.40	$C_{20}H_{40}N_2$	Glyodin, free base
251.5	1.407	$C_{14}H_{24}NO_4PS_3$	Bensulide

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
251.6	1.408	$C_{21}H_{20}Cl_2O_3$	*trans*-Permethrin ($T_t = 170°C$)
252.0	1.415	$C_{12}H_{26}O_6P_2S_4$	Dioxathion (a)
254.5	1.427	$C_{24}H_{38}O_4$	Di-octyl phthalate
255	1.43	$C_{19}H_{11}$	3,4-Benzofluoranthene
257.3	1.447	$C_{10}H_xCl_y$	Halowax 1051 (a)
260.2	1.465	$C_{22}H_{19}Cl_2NO_3$	Cypermethrin
260.6	1.473	$C_{26}H_{23}F_2NO_4$	Flucythrinate (a)
260.9	1.479	$C_{15}H_{19}Cl_3O_4$	2,4,5-T PGB ether esters (a)
261	1.48	$C_{13}H_6Cl_6O_2$	Hexachlorophene
261	1.48	$C_{19}H_{11}$	3,4-Benzopyrene
262.4	1.481	$C_{26}H_{23}F_2NO_4$	Flucythrinate (a)
263.3	1.489	$C_{12}Cl_{10}$	Decachlorobiphenyl
266.0	1.508	$C_{12}H_4Br_6$	Hexabromobiphenyl (a)
266.9	1.513	$C_{25}H_{22}ClNO_3$	Fenvalerate (a)
267	1.51	$C_xH_yO_4$	Hatcol 149 (a)
268.1	1.521	$C_{25}H_{22}ClNO_3$	Fenvalerate (a)
270.9	1.541	$C_9H_{15}Br_6O_4P$	Tris(2,3-dibromopropyl) phosphate
272.9	1.557	$C_{22}H_{19}Br_2NO_3$	Deltamethrin ($T_t = 190°C$)
278	1.59	$C_{22}H_{14}$	1,2,5,6-Dibenzanthracene
282	1.61	$C_{22}H_{12}$	1,12-Benzoperylene
285	1.64	$C_{60}H_{78}OSn_2$	Fenbutatin oxide
286.7	1.660	$C_{16}H_{20}O_6P_2S_3$	Temephos
287.9	1.662	$C_{12}H_4Br_6$	Hexabromobiphenyl (a)

Pesticides and industrial chemicals which produce more than three chromatographic peaks

181.7	0.914	$C_{10}H_6Cl_8$	Chlordane
185.7	0.943	(average)	
191.5	0.984		
196.5	1.019		
203.0	1.066		
206.1	1.088		
212.5	1.133		
218.3	1.175		
129.4	0.580	$C_{12}H_xCl_y$	Aroclor 1221
143.7	0.649		
152.3	0.708		
156.4	0.738		
162.1	0.778		
165.2	0.899		
173.6	0.859		
182.8	0.922		
156.2	0.736	$C_{12}H_xCl_y$	Aroclor 1242
162.2	0.777		
165.0	0.797		
168.6	0.822		
173.7	0.859		
177.0	0.882		
182.5	0.920		
184.5	0.934		
190.1	0.974		
193.2	0.996		
195.0	1.009		

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
200.6	1.047		
203.6	1.070		
156.2	0.736	$C_{12}H_xCl_y$	Aroclor 1248
162.2	0.777		
165.0	0.797		
168.6	0.822		
173.7	0.859		
177.0	0.893		
182.5	0.920		
184.5	0.934		
190.1	0.974		
193.2	0.996		
195.0	1.009		
200.6	1.048		
203.6	1.070		
205.8	1.084		
209.8	1.112		
211.4	1.123		
216.3	1.157		
220.3	1.186		
189.3	0.969	$C_{12}H_xCl_y$	Aroclor 1254
193.0	0.992		
201.0	1.048		
205.8	1.083		
209.9	1.111		
211.6	1.123		
216.4	1.156		
220.6	1.186		
225.1	1.218		
229.0	1.245		
233.4	1.277		
237.0	1.302		
241.1	1.330		
200.9	1.050	$C_{12}H_xCl_y$	Aroclor 1260
205.6	1.083		
211.1	1.121		
216.2	1.157		
220.7	1.189		
222.7	1.202		
224.8	1.218		
228.5	1.244		
232.1	1.269		
236.8	1.302		
240.9	1.330		
243.6	1.349		
248.2	1.382		
251.7	1.407		
201.0	1.050	$C_{12}H_xCl_y$	Aroclor 1262
205.7	1.082		
211.0	1.121		

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
216.2	1.156		
221.0	1.191		
224.9	1.218		
228.6	1.244		
232.2	1.270		
236.9	1.303		
241.1	1.332		
243.8	1.350		
248.4	1.384		
252.0	1.408		
258.3	1.452		
75.0	0.151	$C_{10}H_{11}Cl_7$	Strobane
102.4	0.346	(Average)	
200.0	1.044		
208.6	1.106		
210.4	1.119		
215.5	1.155		
219.3	1.182		
223.5	1.213		
227.9	1.244		
200.2	1.045	$C_{10}H_{10}Cl_8$	Toxaphene
208.8	1.106	(Average)	
212.3	1.130		
215.7	1.153		
219.7	1.182		
223.8	1.210		
228.0	1.241		
233.1	1.276		
236.9	1.303		
239.4	1.320		
119	0.48	$C_{18}H_{13}NO_3$	Naptalam
146	0.67		
154.5	0.722		
240.3	1.325		
127	0.52	$C_{17}H_{24}Cl_2O_4$	2,4-D BEP ester
155	0.72		
185	0.94		
209.1	1.109		
213.6	1.141		
231.3	1.267		
251.9	1.413		
270.4	1.546		
165.0	0.797	$C_{13}H_{19}NO_2$	Bufencarb
171.4	0.843		
173.2	0.855		
177.4	0.884		
214.9	1.148	$C_{26}H_{42}O_4$	Isooctyl isodecyl phthalate
244.1	1.354		
248.1	1.381		

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
258.1	1.451		
267.7	1.520		
218.1	1.171	$C_{20}H_{30}O_4$	Di-isohexyl phthalate
220.5	1.188		
222.5	1.201		
225.3	1.223		
151	0.70	$C_{10}H_xCl_y$	Halowax 1001
168.5	0.823		
175.5	0.872		
183.4	0.927		
186.2	0.947		
190.3	0.976		
194.1	1.002		
196.8	1.021		
168.7	0.823	$C_{10}H_xCl_y$	Halowax 1013
176.0	0.874		
183.4	0.927		
185.8	0.943		
189.9	0.973		
193.6	0.999		
196.3	1.018		
205.7	1.084		
211.2	1.123		
169.4	0.828	$C_{10}H_xCl_y$	Halowax 1014
176.4	0.877		
185.9	0.945		
190.0	0.973		
193.7	0.999		
196.2	1.017		
203.1	1.065		
205.3	1.081		
210.6	1.119		
224.6	1.215		
229.1	1.247		
241.9	1.338		
150.3	0.694	$C_{12}H_xCl_y$	Halowax 1099
168.5	0.822		
175.2	0.870		
180.3	0.905		
183.1	0.925		
185.8	0.944		
189.9	0.973		
193.6	0.999		
196.3	1.018		
206.1	1.086		
211.8	1.126		
168.6	0.822	$C_{12}H_xCl_y$	Halowax 1099-B
175.4	0.871		
185.8	0.944		

TABLE I (*continued*)

T_e	$r_{1/2}$	Formula	Compound
189.9	0.973		
193.7	0.999		
196.2	1.017		
169.2	0.826	$C_{12}H_xCl_y$	Halowax 2141-N
176.2	0.876		
186.0	0.946		
194.1	1.002		
203.4	1.067		
205.7	1.083		
210.1	1.114		
225.1	1.220		
229.5	1.251		
242.0	1.339		
170.1	0.834	$C_{12}H_xCl_y$	Halowax 2148
176.9	0.881		
186.3	0.947		
194.3	1.004		
196.9	1.022		
203.8	1.068		
205.8	1.084		
211.1	1.122		
225.0	1.220		
229.4	1.251		
242.2	1.340		

* Abbreviations: TEPP = tetraethyl pyrophosphate; EPTC = S-ethyl dipropylthiocarbamate; MCPA = 4-chloro-2-methylphenoxy acetate; DNOC = 4,6-dinitro-*o*-cresol; BHC = hexachlorocyclohexane; TBA = trichlorobenzoic acid; BH 584 = 5-chloro-2-isopropylbenzimidazole; MCPB = 4-(2-methyl-4-chlorophenoxy)butyric acid; DCPA = chlorthal dimethyl; TDE = tetrachlorodiphenylethane; MGK 264 = N-octylbicycloheptane dicarboximide; TCMTB = 2-(thiocyanomethylthio)benzothiazole; DDE = dichlorodiphenyl dichloroethylene; DDA, *p,p'*-methyl ester = methyl bis(chlorophenyl)acetate; DEF = S,S,S-tributylphosphorotrithioate; PGB = propyleneglycol butyl; DDT = dichlorodiphenyltrichloroethane; EPN = ethyl *p*-nitrophenyl thionobenzenephosphonate; 4-(2,4-D)B = 4-(2,4-dichlorophenoxy)butyric acid; DEP = butyl ethyl propanediol.

duplicated even though the oven temperatures differ slightly. However, the actual column temperature obtained in some instruments may differ considerably from that indicated on the oven temperature readout and if uncorrected will adversely affect the precision with which many of the values in Table I can be duplicated. The problem can be avoided by standardizing the isothermal temperature of the column midway within the programmed temperature range. A column temperature of 200 ± 1°C can be established by adjusting the isothermal oven temperature to obtain a retention time of 8.14 for *n*-C$_{26}$ relative to *n*-C$_{20}$. Then, when temperature programmed determinations are to be made, the column parameters are normalized so *n*-C$_{20}$ emerges just as the column reaches within ± 1°C of the standardized 200°C temperature. If the detector is insensitive to hydrocarbons, a column temperature of 194 ± 1°C can be established by adjusting the isothermal oven temperature so the retention time of phosalone is 5.7 relative to that of chlorpyrifos.
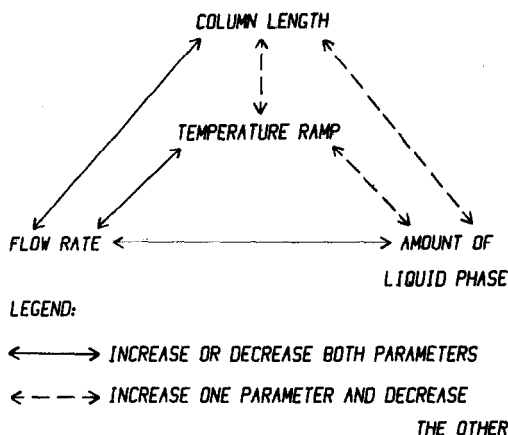
W. L. SAXTON

Fig. 1. A guide for maintaining normalized chromatographic conditions by adjusting one or more parameters to compensate for changes in others. An increase in column length would, for example, require an increase in flow-rate, and/or a decrease in the temperature ramp rate, and/or a decrease in the amount of liquid phase. The amount of liquid phase refers to the weight percent of liquid phase in packed columns or the film thickness in capillaries.

A procedure such as this should be used to standardize column temperatures, irrespective of the type of retention measurement used, whenever the data from one gas chromatograph is to be compared with that obtained from another, especially if the measurements are temperature dependent.

Measurement and use of the intrinsic temperature program rate

Since the temperature program rate is used in the calculation of emergence temperature indices, it must be precisely measured if there is to be close agreement between experimental values and the values listed in Table I. Instead of using the temperature program rate indicated by the gas chromatograph, an experimentally determined intrinsic temperature program rate should be used because it can be more precisely determined from one instrument to another. The intrinsic temperature program rate is the mean rate of increase inside the entire column and can be determined

TABLE II

TYPICAL PARAMETERS FOR METHYL SILICONE COLUMNS NORMALIZED BY SIMULTANEOUS PARAMETER COMPENSATION SO THAT n-EICOSANE EMERGES AT 200 ± 1°C (OR SO THAT CHLORPYRIFOS EMERGES AT 194 ± 1°C)

I.D. (mm)	Length (cm)	Amount of stationary phase	Temperature program rate	Flow-rate
2	110	5%	8.5	30 ml/min
2	180	5%	4.7	35 ml/min
4	120	5%	7.3	65 ml/min
4	180	5%	4	75 ml/min
0.2	1250	0.2 μm	6.8	40 cm/s
0.25	3600	0.2 μm	3.0	31 cm/s

by injecting any pair of compounds listed in Table I which are separated by a considerable temperature difference, and dividing the difference between their tabulated emergence temperature indices by the experimental time interval between them. For example, the difference between the emergence temperature indices of $n\text{-}C_{16}$ and $n\text{-}C_{20}$ in Table I is 89°C. Thus the intrinsic temperature program rate of any column can be determined by injecting these two compounds and dividing 89 by the retention time difference between them. The intrinsic temperature program rate is designated as r' and should be substituted for r in eqn. 1 when emergence temperature indices are to be determined for comparison with those in Table I.

The use of proximal reference compounds

If r' is used in conjunction with reference compounds which emerge in close proximity to the unknown, even better precision can be achieved. However, if the reference compound overlaps the unknown by 50% or more the retention of one or both of the peaks may be altered[8] and the precision of the calculated emergence temperature will be adversely affected. Under the conditions used to obtain the data in Table I, the n-hydrocarbons emerge approximately 18°C apart. Thus the precision of Kovats indices probably can be approached if, for the determination of the emergence temperature indices, a reference is selected which emerges less than 18 degrees from the unknown. The use of proximal reference compounds also enhances the precision with which relative retention times can be determined. However, that precision is generally not as good as for emergence temperature indices[6]. If a proximal reference compound other than chlorpyrifos is used for the determination of relative retention times, they can be calculated by

$$r_{1/2} = r_{3/2} t'_{R1}/t'_{R3} \tag{3}$$

where the subscript 1 refers to the unknown, 2 refers to the reference compound used to obtain the tabulated data, and 3 refers to the proximal reference compound. Thus $r_{1/2}$ is the retention time of the unknown relative to the retention time of the reference compound which was used to obtain the tabulated data (*e.g.*, chlorpyrifos), $r_{3/2}$ is the tabulated relative retention time of the proximal reference compound, t'_{R1} is the adjusted retention time of the unknown and t'_{R3} is the adjusted retention time of the proximal reference compound.

Injection port temperature

During data gathering for Table I, a long needle was used, so that low temperature, on-column injections could be made. This minimized compound degradation. However, a vaporizing injection port can be used if the port is hot enough to vaporize the least volatile compound in the mixture to be analyzed.

Selection of the initial column temperature

Although the initial temperature was set at 50°C to obtain the data for Table I, higher initial temperatures may be used to effect quicker analyses, provided the solutes are cold trapped at the head of the column. Some approximate threshold temperatures[9] (the column temperature at which the solute no longer remains cold trapped and begins moving perceptibly through the column) are listed parentheti-

cally in Table I as a general guide for the maximum initial temperature that can be used. These values were taken from data reported previously[4].

The emergence temperature indices listed in Table I were recorded only to the nearest whole degree if the compounds were not initially cold trapped, because of the difficulty in accurately duplicating the starting temperature with other instruments. Likewise, the relative retention times of those same compounds were recorded to only two significant figures. Agreement can be enhanced for such compounds by using isothermal relative retention times to establish the 50°C starting temperature. The retention of n-C_{11} was 13.6 relative to n-C_8 on the instrument used to gather the data in Table I; hence, when the initial oven temperature is be set at 50°C, it should be set to obtain that relative retention time.

Carrier gas flow-rate

The viscosity of the carrier gas increases as the column temperature increases during PTGC and tends to inhibit the flow-rate. However the gas flow to packed columns is generally regulated by differential flow controllers which tend to maintain a constant flow-rate as the column temperature increases. Indeed, the differential flow controller used to gather the data in Table I did maintain a constant flow.

However, when capillary columns are operated by the usual procedure of maintaining a constant head pressure, the flow-rate will drop considerably as the column temperature rises. For this reason, solutes emerging considerably earlier than the normalization compound, will emerge at a slightly lower temperature than they did when the data in Table I was gathered, and those compounds emerging much later than the normalization compound will do so at a slightly higher temperature. The use of proximal reference compounds and/or the use of r' will compensate for the temperature discrepancy for some compounds but not others, especially if their molecular structures differ considerably from that of the reference compound. Such temperature discrepancies can, however, be minimized if flow programming is used to maintain a constant flow through the capillary column.

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