Gas Chromatography Retention Times and Sensitivity Data for Insecticides and Herbicides

ERNEST J. BONELLI, HAL HARTMANN, and KEENE P. DIMICK

Wilkens Instrument & Research, Inc., Walnut Creek, Calif.

Some of the basic data on pesticides and electron capture gas chromatography are presented, including retention times, sensitivity limits, the concept of linearity, and dynamic range and the voltage–sensitivity–standing current relationship of the concentric tube detector. Also described is the use of two columns which, when combined, form a valuable tool in the resolution, identification, and quantitative determination of several of the commonly used insecticides and herbicides.

Several methods have been employed for the analysis of pesticides. Some of these include the cholinesterase-inhibition analysis, colorimetric and fluorometric procedures, and paper and gas chromatography. In general, these methods, with their elaborate clean-up procedures, are laborious and time-consuming. The advent of more sensitive and specific detection systems, namely the electron capture detector (*6*) and the microcoulometric cell (*2*), have greatly enhanced the gas chromatographic method.

With the increasing importance of gas chromatography in this field of application, the need for basic data is apparent. This paper is intended to provide some of these data in the form of retention times, sensitivity limits, the concept of linearity and dynamic range, and the voltage–sensitivity–standing current relationship of the concentric tube detector. The minimum detectable amounts for the compounds studied ranged from 1 picogram for lindane to 650 picograms for chlorobenzilate. The instrument and two types of column substrates which were used in this analysis are also briefly described.

Apparatus

A Wilkens Aerograph Pestilyzer Model 680 (*5*) equipped with electron capture detector was used for the analysis of the various pesticides. The electron capture detector used is of the concentric tube design as shown in Figure 1. The $^1/_4$-inch kovar tube serves as the cathode and a container for the radioactive source. The source is a 250-mc., cylindrically wrapped titanium tritide foil. The $^1/_{16}$-inch kovar tube also serves a dual purpose—as the anode and a conductor of the column effluent to the detector chamber.

The oven of the apparatus is built of cast aluminum to accommodate the EC detector, $^1/_8$-inch borosilicate glass column, and the injector. The detector temperature is maintained 5° to 10° C. above the oven temperature and thereby reduces surface condensation on the source.

Certain insecticides, notably DDT,

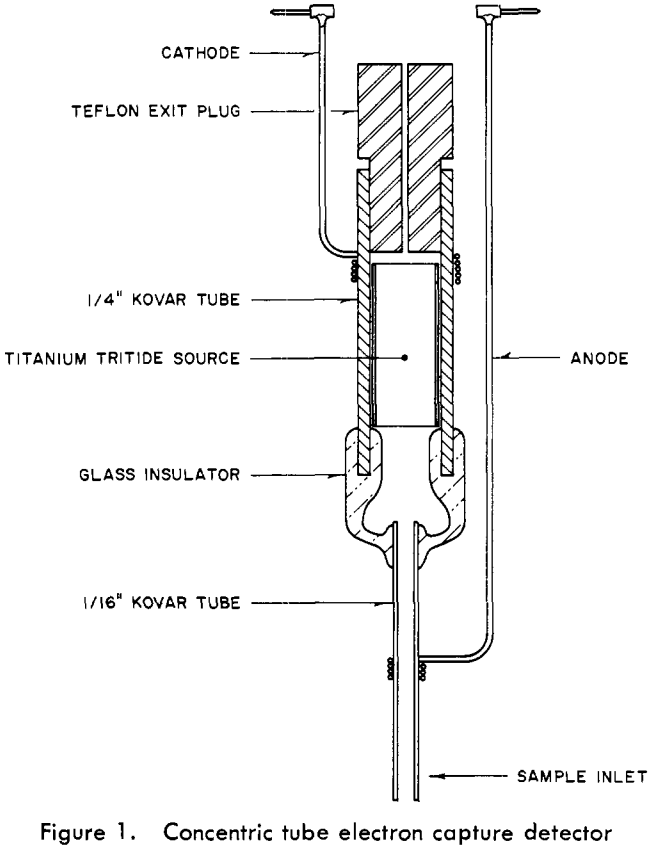


Figure 1. Concentric tube electron capture detector

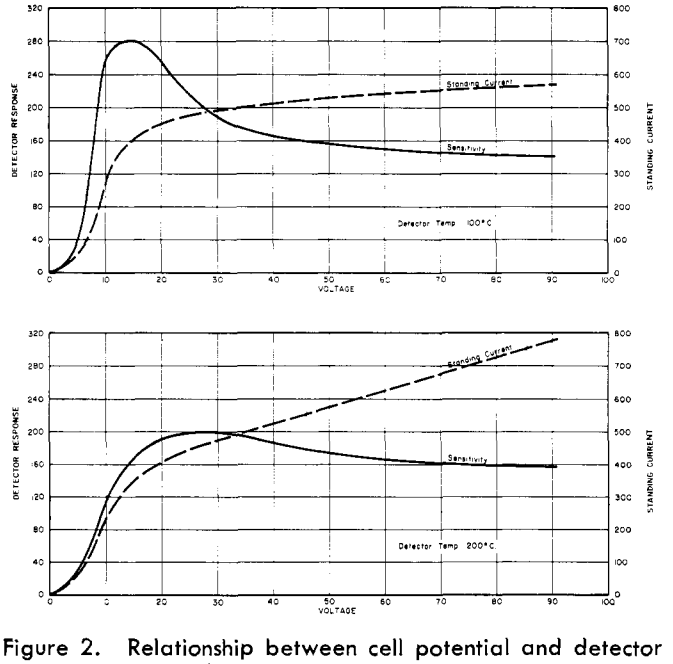


Figure 2. Relationship between cell potential and detector response at two different temperatures

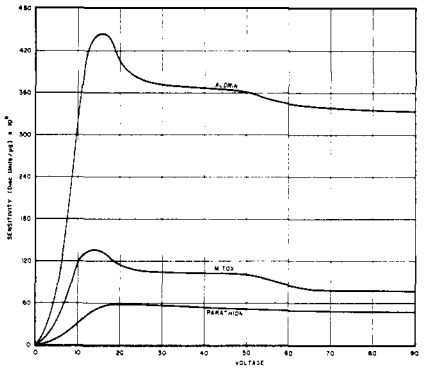


Figure 3. Relationship between cell potential and detector response

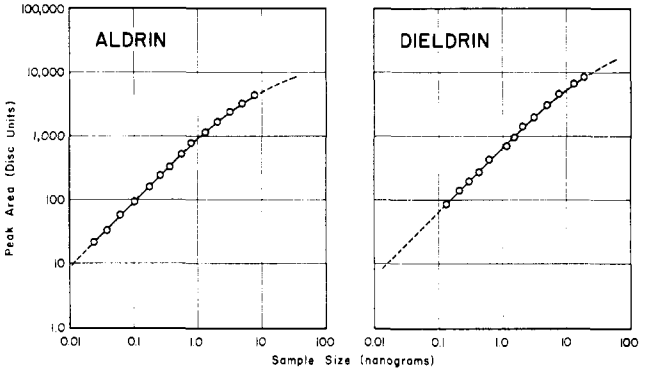
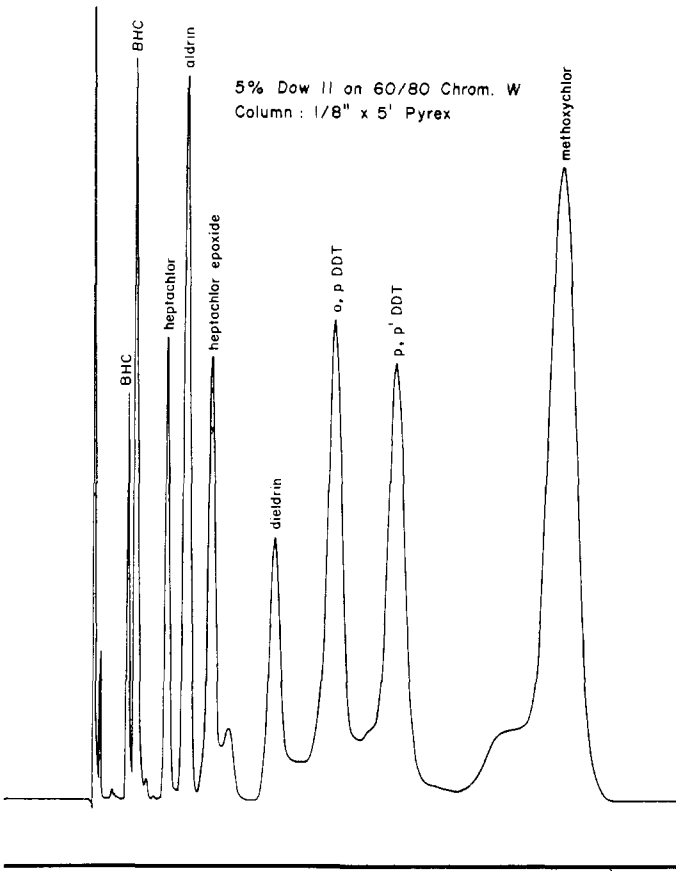


Figure 4. Linearity curve of aldrin and dieldrin



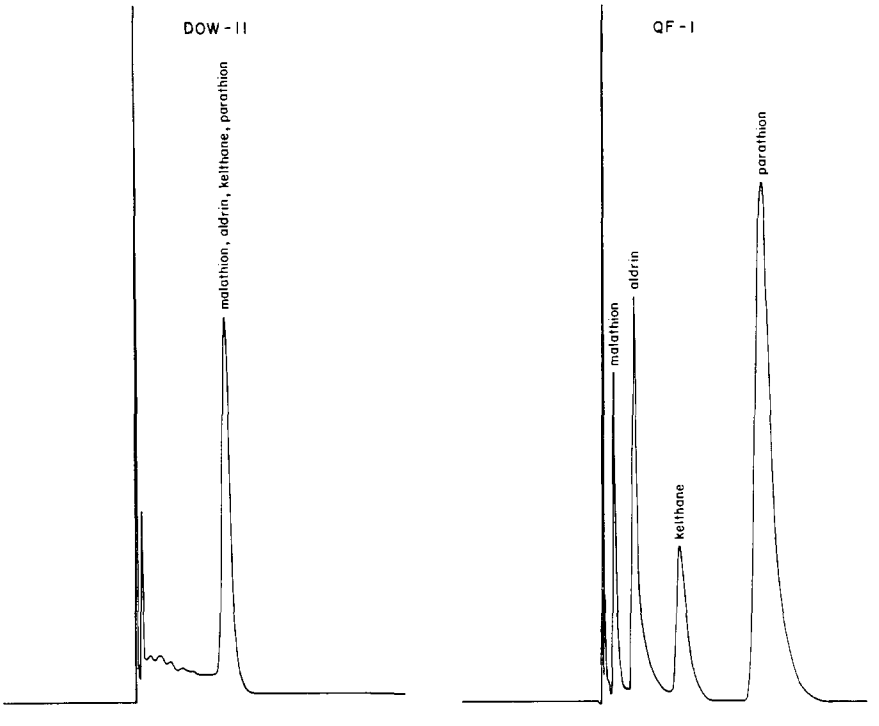


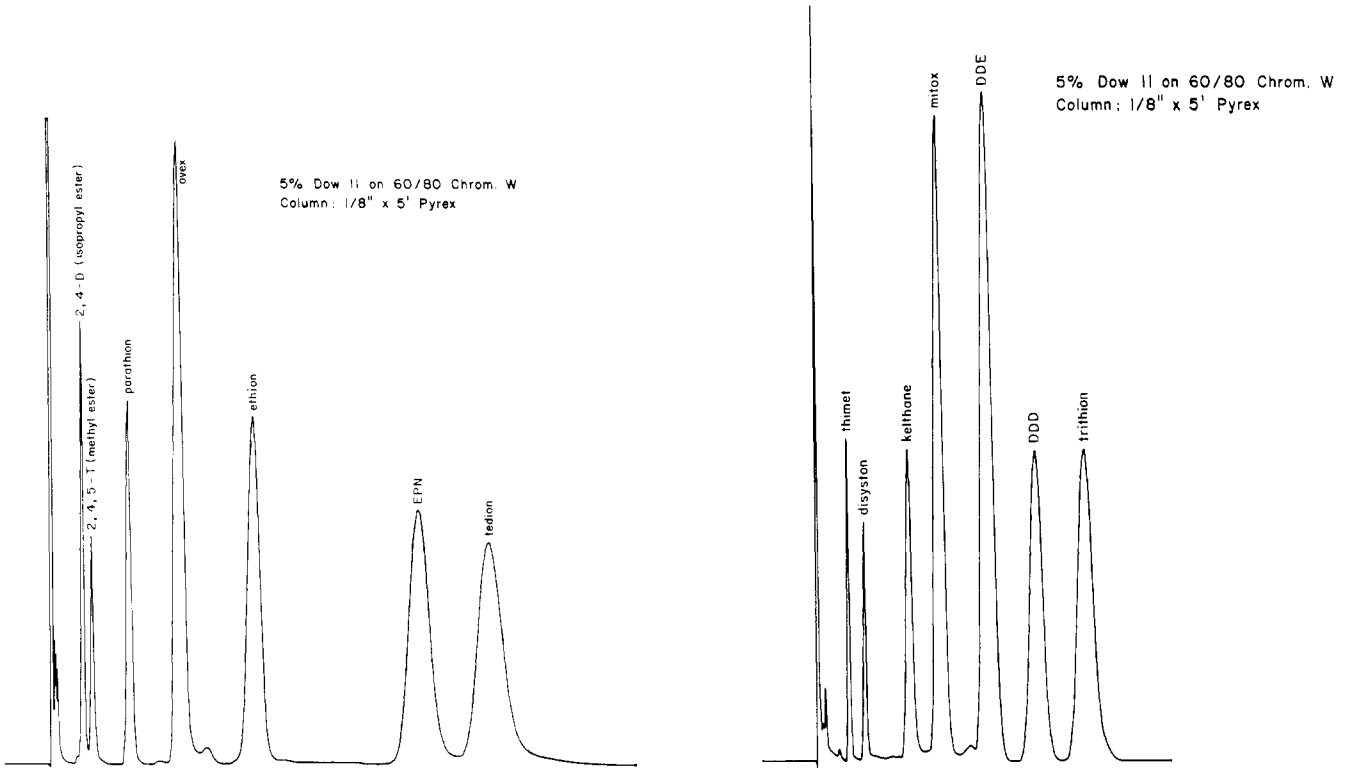
Figure 6. Comparison of a pesticide mixture on QF-1 and Dow-11 columns

are decomposed when they are exposed to hot metal surfaces. To eliminate the problem, a glass tube liner was inserted in the injector (*7*). This completes the all-glass system.

The Pestilyzer is self-contained in that it has within the one cabinet an oven, electrometer, and small tapping recorder. The instrument used in this work, however, was modified by a built-in voltage control with a two-position switch providing 0 to 50 and 0 to 100 volts. This module was inserted in place of the tapping recorder. The chromatograms were recorded with a Brown Recorder connected to the standard plug in the rear of the electrometer.

Voltage–Sensitivity–Standing Current

The relationship between the detector potential, standing current, and sensitivity is materially affected by the detector temperature (Figure 2). At approximately 10 to 20 volts, the sensitivity of the detector at 100° C. is greater than the sensitivity at 200° C. However, at 60 to 90 volts, the temperature variation has essentially no effect on the sensitivity. Neither does the accompanying higher standing current measured at 200° C. have any effect on sensitivity. Depending upon the conditions of the experiment, the sensitivity at the lower voltage varies from one to five times the sensitivity obtained on the



Figures 5. Chromatograms of various pesticide mixtures

plateau (60 to 90 volts). The authors normally operate on this plateau region since a voltage change will not affect the sensitivity of the instrument. This fact, and the nontemperature dependence at 60 to 90 volts, are particular advantages of the concentric tube design.

The chlorinated hydrocarbons, organic phosphorus, and organic sulfur compounds constitute three important classes of insecticides. Figure 3 shows the voltage–sensitivity relationship of representatives of each of these three classes—aldrin, parathion, and mitox. Notice that aldrin, a chlorinated hydrocarbon, is several times more sensitive than the compounds of the other two classes.

Linearity and Dynamic Range

The relationship between sample concentration and detector response is defined as the dynamic range of the detector. The linear portion of the dynamic range is the linearity of the detector. Whenever a new compound is being analyzed and quantitative results are desired, a linearity curve must be obtained. This is made by plotting the detector response versus the sample loading on log-log paper.

Figure 4 shows a linearity curve for dieldrin and aldrin. Generally any compound which absorbs less than 30% of the standing current is said to be within the linear portion of the dynamic range.

Results and Discussion

At this stage in column technology, no one column has been found which will completely separate all the compounds presented to it. For insecticides, the best general purpose columns are the nonpolar silicones, such as Dow-200, Dow-11, and GE SE-30. These materials have been thoroughly explored by researchers using both temperature programming and isothermal conditions.

Some pairs which were difficult to separate with the Dow-11 column are: trithion and *p,p'*-DDT, dieldrin and DDE, sulfenone and mitox, disyston and 2,4,5-T (methyl ester), and lindane and 2,4-D (isopropyl ester). Parathion, aldrin, and malathion (*7*) and kelthane decomposition products are four insecticides with nearly identical retention times. Ethion, DDD (TDE), and *o,p*-DDT are also difficult to resolve. Some of the insecticides which the authors have successfully categorized are shown in Figure 5.

These chromatograms were obtained by using a 5-foot × 1/8-inch borosilicate glass column filled with 5% Dow-11 on 60/80 Chromosorb W. The other operating conditions are: column temperature, 180° C.; injection temperature, 182° C.; detector temperature, 188° C.; detector potential, 90 volts; carrier gas, N_2 at 40 ml. per minute. Under these conditions, all of the compounds studied were eluted within 20 minutes. The only exception is Co-Ral, whose retention time was 36 minutes.

Another column which has served as a valuable aid in the resolution and quantitation is QF-1 (FS-1265). Being a fluorinated silicone and therefore sensitive to electron capture, the QF-1 column must be well conditioned before it can be used. This is best done by placing the coated support in a 100° C. oven for approximately 18 hours. The support is then placed into a column and conditioned for 3 days at 210° to 215° C. prior to use (*4*).

The QF-1 column can separate dieldrin and DDE, trithion and *p,p'*-DDT, and even parathion, aldrin, and the malathion and kelthane decomposition products.

Figure 6 shows the comparison of QF-1 and Dow-11 on the above mixture. It follows that the nonpolar Dow-11 and the polar QF-1 columns combine to form a valuable tool for the analysis of pesticides.

The QF-1 column used here is a 5% coating on 60/80 Chromosorb W, HMDS treated. The other operating parameters are identical to those of the previously mentioned Dow-11 column.

The compounds studied here have been divided into four groups—chlorinated hydrocarbons, organic phosphorus compounds, organic sulfur compounds, and herbicides and miscellaneous compounds.

In Table I, the compounds are cate-

Table I. Chlorinated Hydrocarbons

Compound	Retention Time[a] QF-1	Retention Time[a] Dow-11	Sensitivity[b]	Minimum Detectable Quantity, pg.[c]
Lindane	0.82	0.44	1400	0.1
BHC	0.61	0.36	3600	0.3
	0.82	0.44		
	1.11	...		
Kelthane	2.46	1.0	260	3
p,p'-DDD (TDE)	4.47	2.66	540	4
p,p'-DDE	2.21	1.91	1030	1
p,p'-DDT	4.57	3.26	770	13
o,p-DDT	2.90	2.60	800	7
Heptachlor	0.88	0.80	1010	0.9
Heptachlor epoxide	2.10	1.26	1600	0.9
Aldrin	1.00	1.00	2060	0.4
Dieldrin	3.29	1.94	1600	1
Perthane	2.08	2.30	17	210
Endrin	4.00	2.18	125	70
		2.66		
		4.05		
Methoxychlor	6.00	5.00	172	135
	7.57			

[a] Calculated relative to aldrin as unity.
[b] D.U. per μg. × 100,000 using Wilkens A-680 electrometer at 1× attenuation.
[c] 1 picogram (pg.) = 1 × 10^{-12} gram.

Table II. Organic Phosphorus Compounds

Compound	Retention Time[a] QF-1	Retention Time[a] Dow-11	Sensitivity[b]	Minimum Detectable Quantity, pg.[c]
Methyl parathion	3.88	0.72	128	4
Parathion	5.36	1.0	260	4
Malathion	0.43	1.0	28	60
Ethion	6.23	2.65	314	15
EPN	22.93	4.81	487	13
Trithion	5.40	2.98	670	8
Co-Ral	...	12.4	38	300
Di-Syston	1.00	0.54	19	20
Thimet	0.64	0.35	28	25
Zytron	2.05	0.92	430	5

[a,b,c] Same as in Table I.

Table III. Organic Sulphur Compounds

Compound	Retention Time[a] QF-1	Retention Time[a] Dow-11	Sensitivity[b]	Minimum Detectable Quantity, pg.[c]
Sulfenone	14.67	1.63	425	7
Tedion	26.0	5.72	780	10
Thiodan	3.8	1.61	1800	0.3
	7.9	2.38		
Mitox	2.00	1.37	562	1
Ovex	7.1	1.64	710	2

[a,b,c] Same as in Table I.

Table IV. Herbicides and Miscellaneous Compounds

Compound	Retention Time[a] QF-1	Retention Time[a] Dow-11	Sensitivity[b]	Minimum Detectable Quantity, pg.[c]
2,4-D (methyl ester)	0.81	0.3	160	3
2,4-D (isopropyl ester)	1.14	0.40	179	4
2,4-D (iso-octyl ester)	4.51	2.13	175	5
2,4-DB (methyl ester)	1.72	0.65	25	6
2,4,5-T (methyl ester)	1.43	0.52	1060	0.6
PCNB (terrachlor)	0.88	0.48	2270	0.2
Chlorobenzilate	4.9	2.9	17	650
Binapacryl (dinitro compound)	16.18	2.39	8	310
SD7231 (quinone deriv.)	3.48	1.19	39	33

[a,b,c] Same as in Table I.

gorized according to their relative retention times on each column. In keeping with the precedent set by Coulson (*3*), the retention times are calculated relative to aldrin as unity. In addition, the sensitivity of the individual compounds is in Disc Units per microgram at 1× attenuation using area measurements taken on the Dow-11 column. The minimum detectable quantity is determined by the amount which will give a 10% full-scale deflection at maximum sensitivity. This corresponds to a peak height to noise ratio of 3:1.

A comparison of *p,p'*-DDE and dieldrin shows the versatility of the two columns. On the Dow-11 column, the retention times are essentially the same (1.91 *vs.* 1.94). The QF-1 column easily separates these two compounds (2.21 *vs.* 3.29).

Chlordane and toxaphene give many peaks with both the Dow-11 and QF-1 columns, and are not included in the table. The multitude of peaks due to chlordane and toxaphene would make it very difficult to analyze other pesticides in their presence.

Tables II and III show both the organic phosphorus compounds and the organic sulfur compounds. In general, these two groups of compounds are somewhat less sensitive than the chlorinated hydrocarbons. The organic sulfur compounds owe most of their electron affinity to the chlorine atoms attached to them.

Table IV shows several herbicides and miscellaneous compounds and two chemicals which are sensitive to a group other than halogens. SD-7231 is an experimental insecticide with a quinone structure. Binapacryl is an insecticide which makes use of the dinitrophenyl group to capture electrons.

Acknowledgment

The authors gratefully acknowledge the herbicides given to us by Herman Beckman at the University of California, Davis. They also wish to thank George Jordan, a Wilkens column chemist, and Edward M. Graham for their help.

Literature Cited

(1) Cassil, C. C., "Pesticide Research Bulletin," Vol. **1**, No. 1, Nov. 1961.
(2) Coulson, D. M., Cavanagh, L. A., DeVries, J. E., Walther, B., J. AGR. FOOD CHEM. **8**, 399 (1960).
(3) Coulson, D. M., Huene, A. S., Cavanagh, L. A., Technical Report 1, Stanford Research Institute, Project 3198, October 3, 1960.
(4) DeVries, D., Shell Development Co., private communication.
(5) Hartmann, H., Dimick, K. P., Abstracts, 144th Meeting, Los Angeles, Calif., April 1963.
(6) Lovelock, J. E., Lipsky, S. R., *J. Am. Chem. Soc.* **82**, 431 (1960).
(7) Yeransian, J. A., Mackay, D. A., General Foods Corp., private communication.

Received for review October 1, 1963. Accepted January 27, 1964. Division of Agricultural and Food Chemistry, 145th Meeting, ACS, New York, September 1963.