Analysis of Pesticide Residues by a Dual-Column, Dual-Electron-Capture Detector Method

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A dual-column, dual-electron-capture detector gas chromatographic system for obtaining retention data simultaneously on two different columns with one sample injection is described. Retention data and response characteristics for 17 commonly encountered pesticides are reported. Relative retention times for each column are expressed as a ratio which is independent of column temperature. This system provides reliable qualitative information for the identification of unknown pesticides in minimum time, an extended linearity range for quantitative analysis, plus the separation of some mixtures of pesticides which have similar retention times on one column.

The extremely high sensitivity of electron-capture detectors to chlorinated and certain organophosphate pesticides has led to their acceptance for the gas chromatographic analysis of pesticide residues at the nanogram and picogram levels (Burke, 1963; Burke and Giuffrida, 1964; U. S. Department of Health, Education, and Welfare, 1964). The possibility that plant or animal extractives may contain electron-capturing interferences, the similarities of retention times of some pesticides on a given column, and the lack of specificity of electron-capture detectors to these pesticides makes it desirable to have an independent means of confirming the identity of an unknown pesticide.

The method most often recommended for confirming the identities of unknown pesticides is that of obtaining retention data on several columns with different elution characteristics (Reynolds, 1964). Alternatively, it has been suggested that *p*-extraction values (partition value between two immiscible solvents) be used to identify pesticides (Beroza and Bowman, 1965). Both have disadvantages. If the former method is used, several gas chromatographs should be available, and time is required to make separate injections onto the various columns. If *p*-extraction values are used, they must be determined for several solvent systems to assure identification.

This paper describes a dual-column, dual-detector gas chromatographic system whereby retention data for pesticides can be obtained simultaneously on two different columns with one injection. These retention values plus one *p*-extraction value offer a convenient and reliable method for confirming the identities of pesticides at nanogram and picogram levels. This system offers additional advantages over a conventional single-column system. Pesticides which have identical or similar retention times on one column can often be separated on the other column. The linearity range for quantitative analysis is extended because of the different elution characteristics of the two columns. The retention data from this system can be presented as a ratio of the relative retention times of the two columns, which is essentially independent of column temperature.

EXPERIMENTAL

Apparatus. A modified Varian Aerograph 660 gas chromatograph with a dual-channel electrometer and a Westronics Model LD 11A dual-channel recorder was used for this study. This chromatograph was originally designed for a dual-channel operation with a single column for simultaneous analysis with both a hydrogen flame detector and an electron-capture detector. The modification to a dual-column system with a separate electron-capture detector for each column was made simply by removing the stainless steel 50/50 stream splitter from the column outlet and replacing it at the injector port (or column inlet). Each column was attached to the stream splitter and directly to its respective electron-capture detector (Aerograph concentric tube, tritium source).

This unit was provided with two 5-foot × ⅛-inch o.d. borosilicate glass columns packed with 3% DC-200 on 100- to 120-mesh Gas Chrom Q (Applied Science Laboratories, Inc., State College, Pa.) and 10% QF-1 (fluorosilicone) on 100- to 120-mesh Chromosorb G (Chemical Research Services, Inc., Addison, Ill.). The greater liquid loading on the QF-1 column was necessary to obtain longer retention times on this column than on the DC-200 column. The other operating parameters for this system were: column temperature 190° C.; injector temperature 205° C.; detector temperature 200° C.; detector voltage 90 volts; carrier gas nitrogen at 48 ml. per minute on the DC-200 column and 37 ml. per minute on the QF-1 column. Both columns were conditioned for 3 days at 225° C. with a nitrogen flow rate of 75 to 100 ml. per minute.

Reagents. All solutions were prepared with pesticides of 99+% purity (Chemical Services, Inc., Media, Pa.) in special nanogram quality solvents (Mallinckrodt Chemical Works, St. Louis, Mo.).

Procedure. The retention data listed in Table I were obtained by injecting 1 to 5 μl. of known concentrations of each pesticide in hexane. The retention times are

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Table I. Relative Retention Times and Response Characteristics

Pesticide	RRT[a] DC-200	RRT[a] QF-1	Sensitivity[b]	p-Values[c]
Lindane	0.46	0.82	126.4	0.12
Diazinon	0.51	0.69	2.4	0.28
Methyl parathion	0.72	2.82	10.4	0.02
Heptachlor	0.80	0.90	97.6	0.55
Malathion	0.91	2.67	1.6	0.04
Parathion	0.97	3.62	8.6	0.04
Aldrin	1.00	1.00	100.0	0.73
Heptachlor epoxide	1.26	1.92	80.0	0.29
Thiodan	1.57	2.46	44.8	0.39
Dieldrin	1.86	2.95	88.0	0.33
p,p'-DDE	1.89	2.02	83.6	0.56
Endrin	2.09	3.49	73.2	0.35
p,p'-DDD	2.40	3.54	39.2	0.17
o,p'-DDT	2.54	2.59	63.6	0.47
Ethion	2.57	4.87	5.2	0.08
p,p'-DDT	3.20	3.85	57.2	0.38
Methoxychlor	4.86	5.78	18.4	0.07

[a] RRT. Retention time relative to aldrin at 190° C.
[b] Sensitivity. Peak area in sq. cm./ng. on DC-200 column.
[c] *p*-Values. Partitioning factors for hexane-acetonitrile system.

reported relative to aldrin on each column. The actual retention time for aldrin at 190° C. was 2.6 minutes on the DC-200 column and 2.9 minutes on the QF-1 column. The reproducibility of these relative retention time values for three injections of each pesticide at constant column temperature (190° C.) was ±0.02 RRT. Sensitivity factors and *p*-extraction values are also included in this table. These sensitivity factors can be used for semiquantitative analysis. However, the limited linearity ranges of electron-capture detectors and variations in detector response due to column bleed and the elution of high boiling contaminants make it advisable to prepare response curves for each pesticide. These curves should be checked with standard solutions before each analysis. The *p*-extraction values were determined for a hexane-acetonitrile solvent system. Chromatograms of some pesticide mixtures are illustrated in Figure 1.

The relative retention times on both columns of an unknown compound are compared with those of the known pesticides. If these values match, the pesticide is tentatively identified. If further confirmation is desired, a *p*-extraction value can be determined for the unknown compound and compared to the *p*-extraction value for the known pesticide.

One of the disadvantages of calculating retention times relative to aldrin is that these values vary with the temperature of the column, especially as shown in Table II, for the less volatile pesticides. The ratio of the relative retention times from each column appears to provide values which are fairly constant despite changes in column temperature (Table III). This method of presenting retention data is useful when it is necessary to change the column temperature.

DISCUSSION

A dual-column, dual-detector gas chromatographic system is well suited for obtaining data for confirming the identities of unknown pesticides. However, other features of a dual-column system provide some time-saving and unique advantages for the analysis of pesticide residues.

Because many pesticides have identical or similar retention times on any given column it is often necessary to prepare single columns packed with two different substrates to get a desired separation (Burke, 1965).

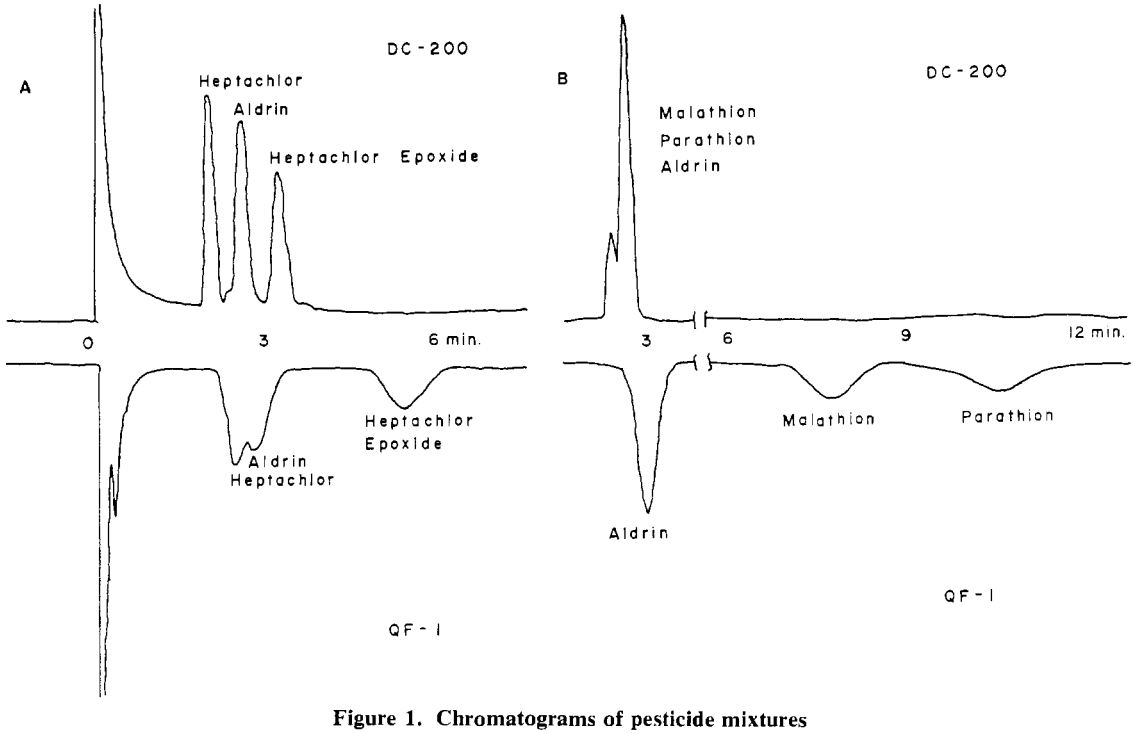

Figure 1. Chromatograms of pesticide mixtures

Table II. Effect of Column Temperature on Relative Retention Times

Pesticide	RRT[a] DC-200			RRT[a] QF-1		
	170° C.	180° C.	190° C.	170° C.	180° C.	190° C.
Lindane	0.45	0.46	0.46	0.79	0.80	0.82
Diazinon	0.52	0.52	0.51	0.72	0.64	0.69
Methyl parathion	0.71	0.74	0.72	3.10	2.95	2.82
Heptachlor	0.77	0.80	0.80	0.86	0.86	0.90
Malathion	0.97	0.93	0.91	3.20	2.85	2.67
Parathion	1.00	1.04	0.97	4.18	3.85	3.62
Aldrin	1.00	1.00	1.00	1.00	1.00	1.00
Heptachlor epoxide	1.28	1.26	1.26	2.02	1.97	1.92
Thiodan	1.62	1.56	1.57	2.62	2.44	2.46
Dieldrin	1.98	1.91	1.86	3.23	3.07	2.95
p,p'-DDE	2.10	1.96	1.89	2.27	2.10	2.02
Endrin	2.22	2.15	2.09	3.87	3.97	3.49
p,p'-DDD	2.68	2.52	2.40	4.05	3.90	3.54
o,p'-DDT	2.87	2.57	2.54	2.92	2.78	2.59
Ethion	2.98	2.72	2.57	6.03	5.18	4.87
p,p'-DDT	3.71	3.39	3.20	4.51	4.07	3.85
Methoxychlor	6.03	5.30	4.86	7.40	6.28	5.78

[a] RRT. Retention time relative to aldrin.

Table III. Ratio of Relative Retention Times of Chlorinated (and Organophosphate) Pesticides

Pesticides	(DC-200/QF-1[a]) 190° C.	180° C.	170° C.	Av.
Methyl parathion	0.26	0.25	0.23	0.25
Parathion	0.29	0.27	0.24	0.27
Malathion	0.34	0.33	0.30	0.33
Ethion	0.53	0.52	0.49	0.51
Lindane	0.56	0.57	0.57	0.57
Endrin	0.60	0.54	0.57	0.57
Dieldrin	0.63	0.62	0.61	0.62
Thiodan	0.64	0.64	0.62	0.63
Heptachlor epoxide	0.65	0.64	0.63	0.64
p,p'-DDD	0.68	0.65	0.66	0.66
Diazinon	0.74	0.69	0.72	0.72
p,p'-DDT	0.83	0.83	0.82	0.83
Methoxychlor	0.84	0.84	0.82	0.83
Heptachlor	0.90	0.93	0.89	0.89
p,p'-DDE	0.94	0.94	0.92	0.93
o,p'-DDT	0.98	0.94	0.98	0.98
Aldrin	1.00	1.00	1.00	1.00

[a] $\frac{\text{Retention time relative to aldrin on DC-200}}{\text{Retention time relative to aldrin on QF-1}}$.

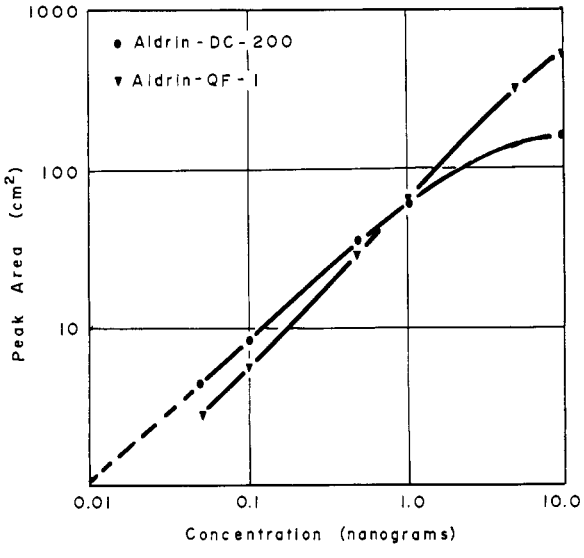

Figure 2. Linearity curves for aldrin

This problem is alleviated with a dual-column system. Pesticides which have identical retention times on one column can often be separated on the other column (Figure 1).

Another advantage of this system is that the linearity range for quantitative analysis can be significantly increased if both columns are calibrated. Because of the greater liquid loading, each pesticide has a longer retention time on the QF-1 than on the DC-200 column. Therefore, the peaks on the QF-1 column are much shorter and broader (Figure 1). This, plus the unequal splitting of the sample, which is again due to the greater liquid loading of the QF-1 column, causes the linearity range of the QF-1 column detector to fall at higher concentrations. The linearity range for the DC-200 column detector for aldrin is from approximately 0.01 to about 0.5 ng. (Figure 2); for the QF-1 column detector, from 0.05 to about 5.0 ng. The total linearity range for both columns is increased by a factor of 10. This can eliminate the necessity to adjust sample size by dilution or smaller injections so that the response will fall in the linearity range of the detector.

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