The Electron Affinity Detector in Pesticide Residue Analysis

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GOODWIN *et al.* (*1*, *2*) determined residues of several insecticides in fruit and vegetables by electron affinity spectroscopy (*3*, *4*). The insecticides were extracted from the crops with acetone and partitioned into hexane. The insecticides in the raw hexane extracts were separated by gas chromatography and determined using a battery-operated, radium beta-ray cell as an electron affinity detector. In the work reported, a similar detector was used to determine residues of insecticides, herbicides, and fumigants in other crops, animal tissues, soils, and miscellaneous plant materials.

Equipment

A Barber-Colman Model 10 double-unit gas chromatograph was used. The detectors were battery-operated, No. A-4071, 6-cc. cells each containing 56 μc. of radium-226. A 90,000-megohm resistor was added to the electrometer to give additional gains of 3000; 10,000;

Table I. Results of Gas Chromatography of Field-Treated Samples

Pesticide	Sample	Extraction Procedure[a]	Column Used	Added P.P.M.	Recovery, %	Sensitivity P.P.M.	Sensitivity P.P.B.	Samples Analyzed
Chlordan	Ontario loam soil	Reynolds	5%, 6 ft.	0.03	93	0.01	...	5
Dieldrin	Alfalfa	Reynolds	5%, 2 ft.	0.08	88	0.02	...	20
	Elm twigs	Skellysolve B surface extraction	5%, 2 ft.	1.0	91	...	...	57
	Ontario loam soil	Reynolds	5%, 2 ft.	0.08	110	...	6	46
	Sandy soil	Skellysolve B surface extraction	5%, 2 ft.	0.50	80	...	...	6
	Elba muck soil	Reynolds	5%, 2 ft.	1.0	60	...	...	6
Endrin	Alfalfa	Reynolds	5%, 2 ft.	0.20	93, 112	0.03	...	5
Heptachlor	Alfalfa	Reynolds	5%, 6 ft.	0.04	72	0.02	...	31
				0.1	80	...	...	...
Heptachlor epoxide	Alfalfa	Reynolds	5%, 6 ft.	0.04	110	...	...	...
				0.1	90	...	1	111
Hexachlorocyclopentadiene (Hooker C-56)	Grapes	Reynolds	20%, 6 ft.	1.0	99	0.02	...	12
Kuron (propylene glycol butyl ether ester of 2,4,5-trichlorophenoxypropionic acid)	Timothy-birdsfoot trefoil quackgrass	Reynolds	5%, 6 ft.	0.3 0.9 3.0	80 80 80	0.04	...	96
Lindane	Loin eye meat	Modified Reynolds procedure	20%, 6 ft.	1.0	98	0.03	...	6
	Leg meat	Modified Reynolds procedure	20%, 6 ft.	1.0	95	0.03	...	6
	Kidney	Modified Reynolds procedure	20%, 6 ft.	1.0	94	0.03	...	6
	Meat fat	Modified Reynolds procedure	20%, 6 ft.	1.0	83	0.03	...	6
	Renal fat	Modified Reynolds procedure	20%, 6 ft.	1.0	90, 92	0.03	...	
	Omental fat	Modified Reynolds procedure	20%, 6 ft.	1.0	102	0.03	...	
	Liver	Modified Reynolds procedure	20%, 6 ft.	1.0	80	0.03	...	6
	Alfalfa	Modified Reynolds procedure	20%, 6 ft.	0.14	90	...	5	17
Nemagon	Cherries	Reynolds	20%, 6 ft.	0.1	88	...	5	15
Telodrin	Alfalfa	Reynolds	5%, 6 ft.	0.024	75	0.01	...	66
				0.4	94	...	...	...
	Ontario loam soil	Reynolds	5%, 6 ft.	0.2	105, 107	...	5	5
Thiodan	Ontario loam soil	Reynolds	5%, 6 ft.	0.1	90	0.01	...	5

[a] There was no additional cleanup.

The simplicity, versatility, and accuracy of the Reynolds procedure for the routine analysis of chlorinated pesticide residues in field-treated samples is illustrated. A Barber-Colman Model 10 gas chromatograph with battery-operated radium detectors was used during a 3-month period to perform over 400 analyses representing 11 pesticides and 15 different samples. The recovery of pesticides was good, and no additional cleanup was necessary following Reynolds extraction of the samples.

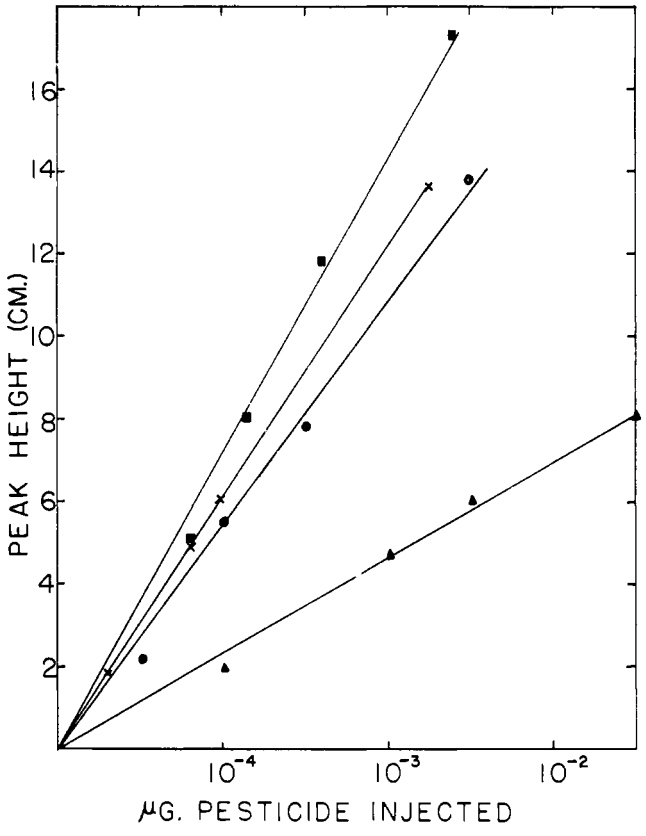

Figure 1. Standard curves of several pesticides by electron affinity spectroscopy

(■ —■ Chlordan, ×—× heptachlor epoxide, ●—● Telodrin, ▲—▲ Thiodan)

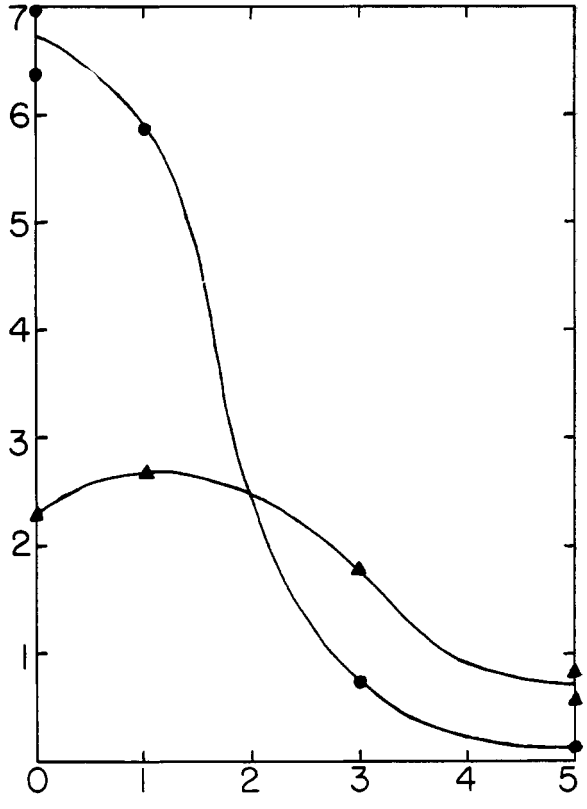

Figure 2. Disappearance of heptachlor and heptachlor epoxide from alfalfa

(●—● Heptachlor, ▲—▲heptachlor epoxide)

and 30,000. The 10,000 setting was most often used during analyses. The recorders were Wheelco, 0 to 50 mv., equipped with 10-inch chart paper, running 10 inches per hour.

Borosilicate glass, U-shaped columns, 9 mm. o.d. and in lengths of 2 and 6 feet were used. The column packing was ethyl acetate–fractionated Dow Corning high vacuum silicone grease on 80–100 mesh, acid-washed Chromosorb W. Columns having either 5 or 20% grease were used. Connections between the column and detector were made with metal hypodermic tubing, glass elbows, and silicone rubber through septums. The operating temperatures for the column, flash heater, and detector were 200°, 265°, and 235° C., respectively, and nitrogen (60 cc. per minute) was the carrier gas. The columns were conditioned for 16 hours at 230° C. before use.

Results and Discussion

Table I lists the results obtained with a number of pesticides in various samples. The samples were analyzed as part of the 1961–62 New York State College of Agriculture's pesticide residue program, in which practical and experimental applications of pesticides were made in the field by the several participating departments of the college.

The extraction procedure of Reynolds (*1*) was used as indicated. It consisted of macerating up to 25 grams of the sample in 65 ml. of acetone in a semimicro Waring Blendor jar for 2 minutes. The solids were filtered out and rinsed with acetone until the filtrate totaled 100 ml. An appropriate portion (5 to 10 ml.) of the filtrate was transferred to a 100-ml. volumetric flask. Ten milliliters of Skellysolve B was added to the flask followed by 2% sodium sulfate to volume. The contents was mixed for 1 minute, and the layers were allowed to separate. A portion of the upper hexane layer was injected into the column using a Hamilton syringe. No further cleanup was required.

The modified Reynolds procedure for extraction of lindane from lamb tissues was as follows. Twenty-five grams of meat or kidney tissue was placed in a mortar with 1 teaspoon of coarse quartz sand and 75 ml. of acetone. The sample was ground vigorously for 2 minutes and the contents rinsed into a 500-ml., round-bottomed flask with 200 ml. of acetone. A three-ball Snyder column was attached, and the mixture was refluxed for 1 hour. The flask was then chilled in ice water and the contents decanted through a plug of glass wool contained in a funnel. The contents on the wool was rinsed with acetone until 150 ml. of filtrate was collected.

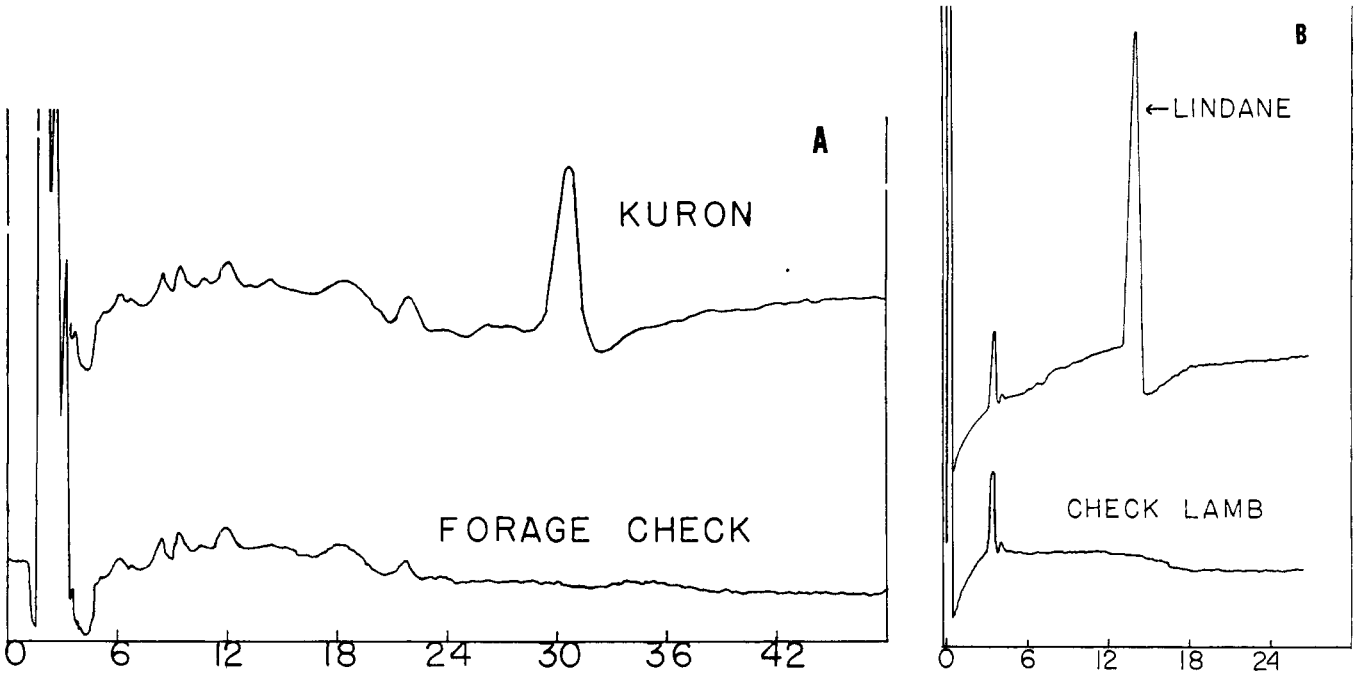

Figure 3. Chromatograms of (A) 0.2 p.p.m. of Kuron recovered from timothy-birdsfoot trefoil forage and (B) 1 p.p.m. of lindane recovered from lamb's liver

A 5-ml. portion of the filtrate was then transferred to a 100-ml. volumetric flask and treated according to the procedure of Reynolds, as described above.

The lamb fat tissues and liver were extracted as described except that it was found necessary to reflux the sample with acetone three times to obtain satisfactory recovery of lindane. In these cases, the sample was chilled in ice water after the first reflux period and the acetone decanted through glass wool. Fresh acetone (100 ml.) was then added to the flask and the mixture refluxed for another hour. Chilling and decanting of this acetone followed before the third refluxing with 100 ml. of acetone and so on. The combined filtrates were made up to 250 ml. after the last reflux and filtering.

The Skellysolve B surface extractions consisted of tumbling the sample for 1 hour with 2 ml. of solvent per gram of sample. The filtered hexane extract was then injected into the column for analysis.

The recovery of pesticides added to samples was calculated after measuring the peak height obtained in the chromatogram. Typical standard curves for several pesticides are shown in Figure 1. The sensitivity was estimated from the smallest amount of the pesticide required to give a 5% full scale deflection above the baseline in the presence of the sample extract. Endrin showed two peaks in the chromatogram, probably having undergone thermal isomerization in the column as previously reported (*6*). The amount of endrin was obtained by taking the sum of both peak heights. Figure 2 shows the disappearance of heptachlor and heptachlor epoxide from alfalfa as determined using the Reynolds procedure.

Figure 3 shows the chromatograms obtained for Kuron added to forage, lindane added to lamb's liver, and untreated samples. The peak heights for Kuron and lindane were 4.2 and 10.6 cm., respectively.

Although the two detectors in the double-unit chromatograph were identical, optimum voltages for electron capture by the chlorinated pesticides were 11 and 22 volts. The detectors were cleaned once a month by rinsing their internal surfaces thoroughly with methylene chloride, chloroform, and ethyl acetate to remove any remaining deposits from column bleeding. The battery voltage to the detectors was kept on overnight, resulting in a stable recorder baseline at the start of each day.

Several standards of a given pesticide were injected each day during analysis. Daily variation in the slope of the curves was very small.

A 20%, 6-foot, silicone grease column had a life of about 2 to 3 months depending on use. The 5% columns and those 2 feet in length had a somewhat shorter life. It was often possible to inject 50 μl. of the sample for greater sensitivity. However, most sample injections were 10 μl. or less.

All of the solvents used were of technical grade, and no further purification was found necessary. Benzene, toluene, hexane, pentane, and diethyl ether produced no adverse effects when used for extraction and injection of samples.

A 1-cc. radium detector (Barber-Colman No. A-4183) as normally used with the Model 20 gas chromatograph was adapted to the Model 10. It performed satisfactorily but was less sensitive by a factor of about 6. This is probably due to the proportionally smaller amount of the pesticide sample present in the detector at one time. Other polyester columns, such as diethyleneglycol adipate on chromosorb, also caused lowered sensitivity. This has also been noted by Mattick (*5*).

It is the authors' opinion that electron affinity spectroscopy is of unparalleled value as a routine tool for determination of chlorinated pesticide residues in field-treated samples. The accuracy and sensitivity of the method are remarkable, and its specificity frees the analyst from the usual tedious cleanup procedures.

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