

Identification and Measurement of Chlorinated Organic Pesticides in Water by Electron-Capture Gas Chromatography

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1817-B



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By WILLIAM L. LAMAR, DONALD F. GOERLITZ, and LEROY M. LAW

ORGANIC SUBSTANCES IN WATER

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*A convenient and sensitive method for
monitoring chlorinated organic
pesticides in water*



UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

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ORGANIC SUBSTANCES IN WATER

IDENTIFICATION AND MEASUREMENT OF CHLORINATED ORGANIC PESTICIDES IN WATER BY ELECTRON-CAPTURE GAS CHROMATOGRAPHY

By WILLIAM L. LAMAR, DONALD F. GOERLITZ, and LEROY M. LAW

ABSTRACT

Pesticides, in minute quantities, may affect the regimen of streams, and because they may concentrate in sediments, aquatic organisms, and edible aquatic foods, their detection and their measurement in the parts-per-trillion range are considered essential.

In 1964 the U.S. Geological Survey at Menlo Park, Calif., began research on methods for monitoring pesticides in water. Two systems were selected—electron-capture gas chromatography and microcoulometric-titration gas chromatography. Studies on these systems are now in progress. This report provides current information on the development and application of an electron-capture gas chromatographic procedure. This method is a convenient and extremely sensitive procedure for the detection and measurement of organic pesticides having high electron affinities, notably the chlorinated organic pesticides. The electron-affinity detector is extremely sensitive to these substances but it is not as sensitive to many other compounds. By this method, the chlorinated organic pesticide may be determined on a sample of convenient size in concentrations as low as the parts-per-trillion range. To insure greater accuracy in the identifications, the pesticides reported were separated and identified by their retention times on two different types of gas chromatographic columns.

INTRODUCTION

The term "pesticide" is exercised to cover a broad class of toxicants that are used to control insects, mites, fungi, weeds, aquatic plants, and undesirable animals. More specific designations include such terms as insecticides, miticides, nematocides, fungicides, rodenticides, herbicides, weedkillers, and defoliant.

Synthetic organic pesticides have introduced a far-reaching technological advance in the control of pests. Although the organic compound DDT (dichlorodiphenyltrichloroethane) was first synthesized in 1874, its insecticidal properties were not discovered until 1939. By 1955, however, more than 100 synthetic organic insecticides were

in commercial use (Nicholson, 1959). As of June 1962, almost 500 chemical compounds incorporated in more than 54,000 formulations were available for use in the United States (President's Science Advisory Committee, 1963). Johnson, Krog, and Poland (1963) reported that in 1962 sales of chemical pesticides at the consumer level reached a record of 1.04 billion dollars and predicted that by 1975 the sales of these toxicants could well reach 2 billion dollars. The predominant trend toward synthetic organic pesticides is expected to continue, especially toward more selective pesticides to control a "target" pest or class of pests and (or) to regulate certain environmental conditions. When pests develop a tolerance to one toxicant, more selective or more toxic poisons are formulated.

Some organic pesticides maintain a residual toxicity for years, whereas others promptly degrade after application. For example, chlorinated hydrocarbon pesticides are generally more persistent and more toxic to fish than the organic phosphorus compounds. The high stability of DDT contributes to its usefulness as an effective insecticide, but this property introduces an environmental contamination problem. After a study to determine the persistence of DDT residues in soils of forest stands which had been heavily sprayed, Woodwell and Martin (1964) reported that DDT residues do accumulate and persist for substantial periods, probably longer than the 10 years previously estimated (Woodwell, 1961). The study by Woodwell (1961) indicated that the ortho-para isomer of DDT is approximately 10 times as persistent as the para-para isomer.

Adequate and convenient identification and measurement of pesticides in water involve complex problems to which there have been many approaches. Procedures have included visible, ultraviolet, and infrared spectrophotometry, paper, column, thin-layer and gas chromatography, and combinations of these tools (Dugan and others, 1963; Goodenkauf and Erdei, 1964; Gutenmann and Lisk, 1964; Hindin and others, 1962; Kahn and Wayman, 1964; Nicholson and others, 1964; Ryckman and others, 1964; Skrinde and others, 1962; and Teasley and Cox, 1963). Rosen and Middleton (1959) reported a procedure for monitoring chlorinated insecticides in water using a combination of carbon-adsorption sampling, adsorption chromatography, and infrared spectrophotometry. The carbon-adsorption method, which involves sample volumes as large as 5,000 gallons, has been applied with various techniques for the analysis of pesticides in water (Bredenbach and Lichtenberg, 1963). However, because the carbon-adsorption method is time-consuming and because recovery tends to be low and (or) quite conditional (Goodenkauf and Erdei, 1964; Grzenda and others, 1964; Hoak, 1964; Ryckman and others, 1964; Teasley and

Cox, 1963; Weber and Morris, 1963a, 1963b; and Wolf, 1963), attention is being given to more direct and highly sensitive techniques which can be performed with a sample of convenient size.

Lovelock and Lipsky (1960) described a sensitive and selective device called an electron-affinity or electron-capture detector. This device, used to detect components as they emerge from a gas chromatographic column, makes possible the selective detection of minute amounts of compounds which have high electron affinities. Inasmuch as chlorinated organic pesticides have high electron affinities, they may be separated and measured in the presence of compounds having low electron affinities. For example, the electron-capturing potential of many of the chlorinated organic pesticides is a million or more times greater than that of hexane.

Electron-capture gas chromatographic systems are now readily available and are being increasingly used for the measurement of extremely low concentrations. Development of more advanced instrumentation and techniques of electron-affinity detection and measurement is in progress (Lovelock, 1963). No one method will be adequate because of the large number of different types of pesticides and also because of the different conditions under which they are present in water. However, the development of electron-capturing procedures for monitoring organic pesticides in water is particularly important because chlorinated and other pesticides with high electron-capturing potentials have the greatest tonnage-use.

In 1964, the U.S. Geological Survey at Menlo Park, Calif., began research on methods for monitoring pesticides in water. Two systems were selected—electron-capture gas chromatography and microcoulometric-titration gas chromatography. These studies are continuing. This report provides current information on advantages, disadvantages, interferences, and application of an electron-capture gas chromatographic procedure.

COLLECTION AND HANDLING OF SAMPLES

The samples are collected in 4-liter glass bottles which have been carefully cleaned and then heat-treated at 300°C overnight to destroy any trace of organic matter (see section on "Interferences"). To avoid airborne contamination, the sample bottle should be stoppered promptly. However, it is important to prevent contact of the sample with rubber, cork, and most plastic (Teflon, a fluorocarbon resin, is satisfactory). Rubber or cork stoppers which have been carefully wrapped with a double layer of organic-free tin or aluminum foil are satisfactory. Care must be taken when stoppering the bottle that the foil covering is not ruptured. The sample should not be transferred from one container to another.

ELECTRON-CAPTURE GAS CHROMATOGRAPHIC METHOD**APPARATUS**

The essential experimental functions— isolation of the chlorinated pesticides and their determination by electron-capture gas chromatography—are performed with the following apparatus:

Gas chromatograph: Aerograph Hy-FI, Wilkens Model 610-C, manual temperature-programming gas chromatograph with electron-capture detector and differential flow controller.

Gas chromatographic oven: Aerograph Hy-FI, Wilkens Model 550, equipped with electron-capture detector, differential flow controller, and detector transfer switch. This additional oven permits use of two different gas chromatographic columns without cooling the oven to change columns.

Gas chromatographic columns: Two columns are used: (1) Dow-11, silicone grease coated 5 percent by weight on 60-80 mesh Chromasorb W (nonacid washed) packed into a 1.5-mm-ID, 3-mm-OD heat-resistant glass column, 5 feet long. (2) QF-1 (also designated FS-1265), fluorinated silicone coated 5 percent by weight on 60-80 mesh Chromosorb W (nonacid washed) packed into a 1.5-mm-ID, 3-mm-OD heat-resistant glass column, 5 feet long.

Recorder: Honeywell Brown Electronik, class 15, 1-riv full-scale response, 1-second pen speed, with a Disc chart integrator.

Sand bath: Tecam fluidized sand bath. A steam bath may be used in place of the sand bath.

Concentrating apparatus: Kuderna-Danish concentrator, 250-ml capacity.

REAGENTS

Anhydrous sodium sulfate: Reagent grade, heated at 400°C overnight and stored in a glass-stoppered bottle. The crystals must be free of electron-capturing material; test by rinsing them with hexane and check the rinsing with the electron-capture gas chromatograph.

n-Hexane: Reagent grade, redistilled from a packed column after being refluxed over bright sodium ribbon for 8 hours and tested to insure that it does not contain significant amounts of interfering electron-capturing components when concentrated 10 times and analyzed as a reagent blank.

Distilled water: See section on "Interferences" for precautions to be observed for preparing organic-free distilled water.

PROCEDURE FOR ANALYSIS

All glassware, except the volumetric, is heat-treated at 300°C overnight to avoid organic contamination. The volumetric glassware is cleaned in the conventional manner with cleaning solution (sodium dichromate in concentrated sulfuric acid). Before they are used, all reagents and glassware are checked for contamination by electron-capture gas chromatography.

1. Extract the pesticides with hexane in such a manner that the water, sediment, and container itself are exposed to the solvent; the following technique is recommended: Pour part of the water sample into a 1-liter separatory funnel and shake with 25 ml of hexane for 1 minute. Allow the contents to separate for at least 10 minutes and collect the aqueous layer in another 4-liter bottle.
2. Repeat this procedure until all the water has been extracted with the same 25 ml of hexane. If the hexane layer becomes partly emulsified, add distilled water to help break the emulsion.
3. Pour the hexane layer from the top of the separatory funnel into a 125-ml Erlenmeyer flask containing 0.5 g of anhydrous sodium sulfate. Allow the sample bottle to drain into the separatory funnel for at least 5 minutes. Rinse the bottle with 25 ml of hexane which is then also poured into the separatory funnel. Several washings made with some of the previously extracted water sample will help transfer the hexane to the separatory funnel.
4. Extract the water a second time with the same 25 ml of hexane used to rinse the sample bottle after the first extraction is completed. Collect the aqueous layer in the original sample bottle, and combine the second hexane extract with the first extract in the 125-ml Erlenmeyer flask. Extract the water a third time with another 25 ml of hexane and add this extract to the first two extracts already in the Erlenmeyer flask. Discard the extracted water after its volume has been recorded to three significant figures.
5. Decant the combined extracts from the sodium sulfate into a Kuderna-Danish concentrating apparatus. Now remove most of the hexane by heating on a fluidized sand bath at 100°C. Transfer the hexane solution quantitatively with a disposable pipette to a 10.00-ml volumetric flask. Bring the solution to volume with hexane and then add about 50 mg of anhydrous sodium sulfate. Mix the contents thoroughly.
6. Take 5- μ l (microliter) aliquots of the sample with a microliter syringe and inject them into the gas chromatograph. The injections are made on both Dow-11 and QF-1 columns to facilitate identification through the different partitioning effects of the two

liquid substrates. The operating conditions for both columns are the same. The glass-lined injection ports are held at 210°–220°C, and the columns are heated at 185°±5°C. Record the exact temperatures at the time of analysis. The nitrogen carrier gas, which is dried by a Molecular Sieve (Linde type 13X), is regulated at 40 ml per minute by differential flow controllers.

- Because the electron-affinity potential of each pesticide may be different, standardization curves must be determined and retained for quantitative analysis. Quantitative and qualitative pesticide standards are injected on the same day the pesticide samples are analyzed to aid in identification and to provide correction, as necessary, for day-to-day fluctuations in the instrument. Retention times are recorded and are summarized in table 1. Relative retention times (the ratio of the retention time of the particular pesticide to that of aldrin) are also given.

TABLE 1.—*Electron-capture gas chromatographic data for pesticide standards*

Pesticide	Dow-11 column		QF-1 column		Response (mv-sec per 10 ⁻¹⁰ g)
	Retention time (minutes)	Relative retention time	Retention time (minutes)	Relative retention time	
Aldrin.....	4.74	1.00	1.58	1.00	94
Dieldrin.....	9.76	2.06	4.84	3.06	97
<i>o, p'</i> -DDT.....	12.90	2.72	4.16	2.63	27
<i>p, p'</i> -DDT.....	16.50	3.48	6.14	3.89	27
Endrin.....	10.80	2.28	5.58	3.53	70
Heptachlor.....	3.74	.79	1.40	.89	71
Heptachlor epoxide.....	6.16	1.30	3.06	1.94	99
Lindane.....	2.18	.46	1.32	.84	98

- The pesticides are identified on two different types of gas chromatographic columns by comparing their relative retention times. The initial identifications are made on a Dow-11 column and the confirmations are made on a QF-1 column. If a closely eluting component interferes with the identification, then, to confirm the identification, a small amount of the pesticide suspected to be present should be added to the sample to be injected into the columns. The injection consists of a measured amount of the pesticide standard drawn into a microliter syringe already charged with an aliquot of the sample extract.

INTERFERENCES

The experimental studies showed that lindane present in the injected sample in amounts as low as 0.1 picogram (1 picogram=10⁻¹² gram) can be readily detected and measured. The degree of sensitivity varies with the electron affinity of the particular compound and also from

one instrument to another. High sensitivity requires meticulous laboratory techniques and high-purity reagents. Trace contamination by compounds with high electron-affinity potentials should be avoided, but other contaminants do not seriously affect the results.

When this investigation started, all glassware in the laboratory was discovered to be contaminated extensively with interfering organic compounds. The contamination was largely due to distilled water used for rinsing the glassware. The distilled water was obtained from a high-purity still that had no provision for removing organic material from the feedwater, but most of the organic contamination actually was coming from the valves, gaskets, connections, piping, and the storage system, and possibly from the pump used to pump the water to the storage tank. This contamination may be remedied by collecting the distilled water directly from the condenser exit. Depending on the quality of the feedwater, it may be necessary to use a high-purity still with an organic remover on the feedwater.

A more convenient and satisfactory distilled-water system is a gravity one that consists of a high-purity still with an organic remover (activated carbon) on the feedwater, a tin-lined or tin-silver-lined storage tank having an ultraviolet lamp, and tin-lined piping, valves, and connections. If some plastic must be used in the system, Teflon, a fluorocarbon resin, is satisfactory. High-purity (organic-free) distilled water may be also obtained by redistilling good quality distilled water over alkaline permanganate in an all-glass system.

Each laboratory will have to insure that the sample bottles and all glassware used in the analysis are free of electron-capturing contaminants. Rinsing the glassware with solvents will remove organic contaminants, but the effectiveness of this removal apparently varies inversely with the degree of adsorption. For example, contaminated glassware was rinsed with hexane until the analysis of these rinsings indicated no contamination, but this hexane-rinsed glassware again contaminated hexane which remained in it overnight. The authors found that heat-treating the glassware (including sample bottles but not volumetric glassware) at 300° C overnight is the most convenient way to avoid contamination from organic matter. As a further precaution, the glassware should be solvent-rinsed and checked by electron-capture gas chromatography prior to use.

Reagents as presently obtained on the market, including chromatography quality reagents, are usually not pure enough for use in electron-capture analysis. ACS-grade or chromatography quality hexane can be further purified by refluxing it over bright sodium (freshly prepared sodium ribbon). However, the quality of the hexane solvent may vary from bottle to bottle, and therefore this treatment is not always adequate.

Another possible significant source of contamination, which might be termed the "screw-cap effect," is the plastic screw caps used on sample bottles and reagent bottles. Even if the plastic cap itself does not cause contamination, the liner on the cap may do so. For example, during the investigations the anhydrous sodium sulfate used in drying the solvent was found to be contaminated. In tracing the source, it was established that the screw-cap liner had contaminated the sodium sulfate. Impurities from this source can be avoided by heat-treating the sodium sulfate at 400° C overnight and by storing it in an all-glass container.

High-purity nitrogen carrier gas is required for direct-current electron-capture detectors. This gas should be filtered and dry. Particular attention should be given to the efficiency of the drying agent because an exhausted drier will allow the passage of water, thus reducing the standing current.

RESULTS AND SUMMARY

The experimental results obtained by the use of this method cover a variety of waters. These include waters from streams that were analyzed for chlorinated organic pesticides and both distilled water and stream samples to which the pesticides were added for recovery tests.

In the recovery studies, two techniques of introducing the pesticides into the water were investigated—hexane solutions and emulsion suspension:

1. Addition of pesticides from nonaqueous solution such as a hexane solution, is a very convenient technique that is frequently used by many workers in this field, but investigations indicated that this technique is not acceptable because the recovery of the chlorinated organic pesticides after they were added to distilled water was low, ranging from 54 to 87 percent. Many chlorinated hydrocarbon pesticides are not very soluble in water. A true solution is probably not immediately achieved when they are added to water in hexane solvent. The suspension assumed to take place is not uniform and, even in samples having concentrations in the parts-per-trillion range, the rate of solution is not rapid enough. Handling and processing nonuniform suspensions also introduce problems.
2. Because the hexane-solution technique did not provide satisfactory recovery, a procedure using emulsifiable pesticide concentrates was developed. Microliter quantities of emulsifiable concentrates of aldrin, DDT, dieldrin, endrin, heptachlor, and lindane were added to distilled water. Portions of each suspension were serially diluted, and the concentration of the pesticide in the final diluted

suspension was determined by gas chromatography; vigorous mixing prior to sampling obviated measurable phase separation. Appropriate amounts of the pesticides were added to 4 liters of distilled water. Recovery experiments were performed on these prepared samples using the developed gas chromatographic method. These results, expressed in nanograms (1 nanogram = 10^{-9} gram), are shown in table 2. From these data, it is concluded that addition of pesticides to water as standardized-emulsion suspensions is acceptable.

TABLE 2.—*Recovery of pesticides from distilled water after addition as an emulsion*

Test	Pesticide	Quantity added (nanograms)	Recovered	
			Nanograms	Percent
1.....	Aldrin.....	1,100	980	89
	Dieldrin.....	940	960	102
	Heptachlor.....	880	735	84
	Lindane.....	1,210	1,225	101
2.....	Aldrin.....	1,100	970	88
	Dieldrin.....	940	910	97
	Heptachlor.....	880	720	82
	Lindane.....	1,210	1,150	95
3.....	Aldrin.....	1,274	1,320	104
	Dieldrin.....	1,156	1,200	104
	Heptachlor.....	127	130	102
	Lindane.....	1,401	1,600	114
4.....	DDT ¹	5,100	5,000	98
5.....	DDT ¹	3,773	3,850	102
	Endrin.....	980	1,000	102

¹ Summation of *o,p'*-DDT and *p,p'*-DDT.

To study the reliability of the gas chromatographic method on unfiltered surface-water samples and to document the stability of pesticides with respect to time, additional recovery experiments were performed. Three samples from each of the different streams were collected in 4-liter bottles. Known amounts of the standardized-pesticide emulsion were added to two of the samples of water; the remaining sample of water was used as the blank. All three samples of water were analyzed by the gas chromatographic procedure; the blank and one sample containing the added pesticides were analyzed immediately, but the other sample containing the added pesticides was analyzed 30 days later to determine the stability of the pesticides.

The data on the recovery of the pesticides are shown in table 3. All the results are satisfactory except that for heptachlor recovered 30 days later. Whereas the recovery of the heptachlor immediately after addition was satisfactory, no heptachlor nor its conversion product, heptachlor epoxide, was found 30 days later. (Bowman and others, 1964, reported the conversion of heptachlor to heptachlor epoxide as a metabolite in mosquito larvae, but this conversion did not occur in the aqueous suspensions.)

TABLE 3.—*Recovery of pesticides from selected water samples after addition as an emulsion*

Source	Pesticide	Quantity added (nanograms)	Recovered			
			Immediately		30 days later	
			Nano-grams	Per-cent	Nano-grams	Per-cent
Columbia River at Vancouver, Wash.....	Aldrin.....	296	280	95	344	116
	DDT ¹	1,159	1,320	114	941	81
	Dieldrin.....	229	236	103	242	106
	Endrin.....	289	224	78	223	77
	Heptachlor.....	408	500	123	0	0
	Lindane.....	174	182	105	155	89
Yuma Main Canal at Yuma, Ariz. (water diverted from Colorado River at Imperial Dam).	Aldrin.....	296	316	107	310	105
	DDT ¹	1,159	1,378	118	1,316	114
	Dieldrin.....	229	247	108	249	109
	Endrin.....	289	237	82	247	85
	Heptachlor.....	408	490	120	0	0
	Lindane.....	174	198	114	151	87
Colorado River at Lees Ferry, Ariz.....	Aldrin.....	296	300	101	280	95
	DDT ¹	1,159	1,220	105	1,096	95
	Dieldrin.....	229	234	102	241	105
	Endrin.....	289	234	81	227	79
	Heptachlor.....	408	500	123	0	0
	Lindane.....	174	178	102	147	84

¹ Summation of *o*, *p*'-DDT and *p*, *p*'-DDT.

The analytical procedure described was applied to the determination of chlorinated organic pesticides in unfiltered samples of water collected from streams in several States, and the results are given in table 4. To provide confidence in the results, all identifications were made on two different types of gas chromatographic columns: Dow-11 and QF-1. A pesticide identified on one column but not confirmed on the other column was not reported in the results.

In this research, 4-liter samples were used, but smaller samples can be used in routine analysis. Most sources of contamination in the laboratory can be eliminated by precautions described in the section on "Interferences." Electron-capturing compounds (other than the pesticides) are present in some industrial wastes, and if these wastes are present in the water samples to the extent that they interfere with the analysis, either clean-up procedures or other methods of analysis will be necessary. Thus far, however, natural organic matter and agricultural pollution have not produced an interference problem in this research.

This method is a convenient and extremely sensitive procedure for the identification and measurement of organic pesticides having high electron affinities. Because chlorinated organic pesticides have high electron affinities, they can be separated and measured in the presence of compounds having low electron affinities. For example, the electron-capturing potential of many of the chlorinated organic pesticides is a million or more times greater than hexane.

TABLE 4.—*Electron-capture gas chromatographic analysis of chlorinated pesticides in unfiltered samples of surface water*

Source	Location	Date collected (1964)	Pesticide found	Concentration (parts per trillion)
Alamo River.....	Near Niland, Calif.....	Feb. 5	Dieldrin.....	70
New River.....	Near Westmoreland, Calif.....	Feb. 5do.....	50
Black River tributary No. 1.	Near Bangor, Mich.....	May 13do.....	<10
			Heptachlor epoxide.....	<10
			Lindane.....	10
Mill Creek.....	Near Hartford, Mich.....	May 13	Dieldrin.....	10
			Heptachlor epoxide.....	<10
			Lindane.....	<10
Brazos River.....	Near College Station, Tex.....	Sept. 18	Aldrin.....	10
			Endrin.....	20
			Toxaphene.....	1,140
Colorado River.....	Near Wharton, Tex.....	Sept. 19	Dieldrin.....	<10
			Lindane.....	<10
Ohio River.....	At Cincinnati, Ohio.....	Sept. 28	Aldrin.....	20
			Endrin.....	40
			Heptachlor epoxide.....	10

Measurable losses due to adsorption of the pesticide on the walls of the sample container are obviated because the walls of the container are exposed to the solvent. The recovery of the individual pesticides was good, average recoveries ranging from 89 to 104 percent. By this method, the pesticides may be determined on a sample of convenient size in concentrations as low as the parts-per-trillion range. This procedure has practical applications in surveillance programs, especially if prompt information or action is needed.

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