Use of Granulated Zinc Columns for Determining Chlorinated Organic Insecticides

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As a measure of the insecticide present, the chlorine content of chlorinated organic insecticides is often determined. A simple procedure has been developed for the partial or complete removal of the organically bound chlorine as chloride ion by the percolation of an acidified solution of the insecticide through a granulated zinc column. The fraction of the chlorine removed as chloride ion is a function of the molecular structure of the compound and is a reproducible value for a given insecticide. The chloride ion liberated is determined by potentiometric titration with silver nitrate. Applied to formulations and technical products, the procedure has a degree of specificity not available in analyses dependent on total chlorine determinations.

METHODS FOR CHLORINATED ORGANIC INSECTICIDES are not always available or readily applicable. All or a part of the organically bound chlorine is often determined as a measure of the amount of the insecticide present. Total chlorine may be determined by direct combustion (1) or sodium reduction (2, 3, 6). Partial-dechlorination methods generally depend on determining the alkali-labile chlorine present in a molecule (4).

A simple procedure is described here for removing all or a fraction of the chlorine, depending on the nature of the molecule, in a compound as chloride ions by slowly percolating a solution of the compound through a column of granulated zinc.

Procedure

Apparatus A borosilicate glass column was made from tubing with an outside diameter of 22 mm. and about 415 mm. long. A stopcock was fused to the bottom of the tube.

A Fisher Titrimeter was used for the potentiometric determination of chloride ion.

Reagents Acetone, ACS grade, redistilled.

Acetic acid, glacial.

Acetic acid, 10% (v./v. water).

Acetone-acetic acid wash. (Prepared by mixing 2 volumes of acetone with 1 volume of the 10% acetic acid.)

Zinc, 20-mesh.

Silver nitrate, 0.1 N (standardized).

Nitric acid, concentrated.

Column Preparation The column in which dehalogenation takes place is prepared by placing a wad of glass wool at the base of the 22-mm. tubing, just above the stopcock. Two hundred grams of 20-mesh zinc, conditioned by leaching in 10% acetic acid for 2 hours with occasional stirring, is poured into the column. Zinc adhering to the sides of the column is washed down with 10% acetic acid. The acid is drained until the liquid level reaches the top of the zinc. The column is then washed with two successive 75-ml. portions of the wash solution and is ready for use.

Sample Preparation **Unformulated Insecticide.** From 100 to 200 mg. of the chlorinated insecticide is placed in a 150-ml. Erlenmeyer flask and dissolved in 50 ml. of acetone; 25 ml. of the 10% acetic acid is then added.

Formulated Dusts. A sample containing 100 to 200 mg. of insecticide is extracted with 20 ml. of acetone by gentle refluxing on a steam bath for 10 minutes. The residue is allowed to settle and the supernatant liquid decanted through a fritted-glass suction filter into a 150-ml. Erlenmeyer flask. The extraction is repeated three times. The volume of the combined filtrates is reduced to 50 ml. on the steam bath and the solution is allowed to cool to room temperature. Then 25 ml. of 10% acetic acid is added.

Liquid Formulations. A sample containing 100 to 200 mg. of the insecticide is diluted to 50 ml. with acetone in a 150-ml. Erlenmeyer flask, and 25 ml. of 10% acetic acid is added.

Dehalogenation The clear solution of the sample is poured into the column and allowed to drip slowly into a 400-ml. beaker at a rate of flow such that the liquid level descends to the top of the zinc in approximately 1 hour. The rate of flow is regulated by means of the stopcock. The Erlenmeyer flask is rinsed with 25 ml. of the acetone-acetic acid wash and the rinse added to the column. The same flow rate is maintained. When the liquid level again descends to the top of the zinc, another 50 ml. of wash is added, followed by a third wash of 75 ml. After this last addition the flow rate is increased by regulation of the stopcock so that the entire 75 ml. enters the zinc column in 15 minutes.

Chloride Determination The resulting quantity of chloride ions is determined by a potentiometric titration (5). To the eluate in the beaker, 75 ml. of distilled water and 5 ml. of concentrated nitric acid are added and the contents are titrated with 0.1 N silver nitrate. The quantity of chloride ion found, corrected for the blank, multiplied by the appropriate factor, gives the quantity of the insecticide in the sample. The blank should be determined for each analysis by preparing the same sample weight used in the analysis exactly as described under sample preparation, then, without percolating the solution through the column, adding 150 ml. of wash solution, 75 ml. of distilled water and 5 ml. of concentrated nitric acid and determining the chloride ion. Conversion factors are obtained by analyzing, in exactly the same manner, 100 to 200-mg. samples of the pure materials. Where mixtures occur, as in toxaphene and Strobane, the factor is obtained by averaging the results for several representative samples. This would not give an absolute value but where no methods other than chloride are available this method is useful. Dividing the weight of the pure sample taken by the weight of chloride ions found, gives the conversion factor for the insecticide.

Discussion

Zinc has been used to form olefins by dechlorinating 1,2-dihalides, to prepare

Table I. Per Cent Chlorine Removable and Factors for Conversion of Milligrams of Chloride to Milligrams of Insecticide

Material[a]	Definition	Chlorine atoms in molecule	Per Cent Chlorine Total	Per Cent Chlorine Removable	Conversion factor
Lindane	Gamma isomer of BHC (1,2,3,4,5,6-hexachlorocyclohexane) of not less than 99% purity	6	73.1	73.1	1.367
Technical BHC	1,2,3,4,5,6-Hexachlorocyclohexane, consisting of several isomers and containing 12 to 14% of the gamma isomer	6	73.1	73.1	1.367
Methoxychlor	1,1,1-Trichloro-2,2-bis(p-methoxyphenyl)ethane	3	30.8	25.2	3.963
Toxaphene	Chlorinated camphene having chlorine content of 67–69%	ca. 8	67–69	42.5	2.332
Strobane	A terpene polychlorinate with a chlorine content of approximately 66% (chlorinated α-pinene isomers)	ca. 8	66	36.2	2.760
p,p-DDT	1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane	5	50.0	25.2	3.963
DDT	Commercially available dichlorodiphenyltrichloroethane, the principal constituent of which is 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane				
Chlordan	1,2,4,5,6,7,8,8 - Octachloro - 3a,4,7,7a - tetrahydro - 4,7 - methanoindan	ca. 8	69.2	25.2	3.963
Heptachlor	1(or 3a), 4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	7	66.5	19.7	5.097
Aldrin	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,endo,exo-5,8-dimethanonaphthalene	6	58.3	13.2	7.600
Dieldrin	Not less than 85% of 1,2,3,4,10,10-hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a - octahydro - 1,4 - endo,exo - 5,8 - dimethanonaphthalene	6	55.9	12.4	8.052
Bayer L 13/59	O,O-Dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate	3	41.4	26.5	3.776
DDVP	Dimethyl 2,2-dichlorovinyl phosphate	2	32.1	0	...
Carbon tetrachloride		4	92.2	85.2	1.174
Ethylene dichloride		2	71.7	0	...
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene	4	44.4	0	...
2,4-D	2,4-Dichlorophenoxyacetic acid	2	32.1	0	...
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid	3	37.6	0	...

[a] All compounds listed were purified samples except technical BHC, toxaphene, strobane, chlordan, and DDT, which were of necessity technical grade products.

Table II. Per Cent of Insecticide in Commercial Formulations

Formulation	On Label	Found Total chlorine	Found Zinc reduction
Toxaphene dust	25.0	22.7	23.4
Toxaphene emulsion concentrate	60.0	60.2	60.5
Methoxychlor emulsion concentrate	25.0	26.2	25.8
DDT emulsion concentrate	25.0	27.3	25.2

cyclic compounds from alpha, omega-dihalides, and to replace halogens by hydrogen (7).

The rate of chlorine removal will vary not only with the type of reaction but also with the group adjacent to any particular chlorine atom. Under the dechlorination conditions described, vinyl chlorides will not react—e.g., DDT, 2,4-D, and 2,4,5-T (Table I)—because resonance stabilization makes the chlorine inert. Adjacent chlorines in ethylene dichloride react slowly, if at all, but those in hexachlorocyclohexane are readily removed to form benzene.

No detailed study was made of the reaction products other than the chloride ion formed during the reaction. The percolation time was long enough to give maximum consistent values obtained at room temperature using the procedure described. However, the chlorinated hydrocarbon insecticides in use today contain from two to eight chlorine atoms per molecule and the number of different kinds of molecules that may be formed, even from a pure compound, in the course of the dechlo-

rination reaction may be many, and the probability of removing all the chlorine by this technique is rather poor. However, the experimental conditions chosen are such that the over-all reaction yields reproducible empirical factors that can be used to correlate the quantity of chloride ions obtained from the chlorinated insecticide with the amount of that insecticide originally present. As in other methods depending on partial or total chlorine determinations, a qualitative knowledge of the chlorinated organic compounds present is necessary before any quantitative estimates can be made.

The recoveries of known amounts of insecticide were best for lindane where recoveries were within the range 100 ± 0.2% and were poorest for chlordan where recoveries were within the range 100 ± 2.0%. As a check on the method, the per cent chlorine removed by this procedure from the beta and delta isomers of benzene hexachloride and from toxaphene and Strobane was compared with that chlorine removed by refluxing for 2½ hours with 30-mesh zinc in glacial acetic acid. The zinc

column dechlorinated the beta and delta isomers completely while only 80% and 30%, respectively, of the chlorine was removed by zinc in glacial acetic acid. The corresponding figures for toxaphene were 42.5% versus 34% and for Strobane 36.2% versus 31%. The higher figure in each case was obtained by the use of the zinc column.

With the aid of the factors in Table I, a number of formulated products were analyzed. Table II compares the results obtained from a government laboratory that checks the contents of the sample with the label claims, with those obtained by the standard sodium–isopropyl alcohol total-chlorine method.

The data presented in Table I represent the maximum per cent chlorine removed by this technique under the conditions described. Conditions were chosen to ensure maximum accuracy and reproducibility and to minimize small differences in the reaction rates. However, by substituting less active metals such as iron, tin, or amalgamated zinc, and by using solvents with pH values closer to neutrality, it is possible to bring out fine distinctions that in special cases may be useful.

Different conditions of pH and column material will affect the relative rate of dechlorination. As an example, the various isomers of hexachlorocyclohexane react quantitatively with granulated zinc and 10% acetic acid, as described in the procedure. For the purpose of this study drastic conditions were selected in order

to obtain maximum dechlorination. However, additional information may be gained by varying experimental conditions as shown in the following example, which illustrates the possibilities of the method. The chloride recovery for the different isomers from a 200-gram amalgamated-zinc column and a solvent consisting of 2 parts of acetone to 1 part of a sodium acetate–acetic acid solution buffered at pH 4.8 was found to be as follows: alpha 11.9, beta 0.9, gamma 99.5, and delta 0.9%. The beta and delta isomers are practically inert, but dechlorination of the gamma isomer proceeds almost to completion. Unfortunately, the alpha isomer dechlorinates enough so that this method of analysis cannot be used for determining the gamma content of technical BHC.

Conclusions

The major advantages of the procedure outlined are extreme simplicity and a degree of specificity not available in analyses dependent on total-chlorine determinations. For example, toxaphene may be determined in the presence of 2,4-D and 2,4,5-T, the DDT content of a sample of DDT containing DDE can be estimated rather readily, and any titratable chloride ion is a measure of contaminating materials in DDVP.

The method may perhaps be most useful for materials, such as lindane and technical BHC, that are completely dechlorinated, and for materials, such as toxaphene and Strobane, for which specific methods are not yet available.

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HERBICIDE RESIDUES

Residues in Crops Treated with Isopropyl N-(3-Chlorophenyl)carbamate and Isopropyl N-Phenylcarbamate

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The analytical method for the measurement of isopropyl N-(3-chlorophenyl)carbamate in experimental field plots is applied to grapes, tomatoes, carrots, sweet potatoes, strawberries, and peaches; peas were tested for isopropyl N-phenylcarbamate residue. Average recovery of added values of the herbicides to untreated crops was about 89% by this method. Results show that the harvested crops which had been treated with isopropyl N-(3-chlorophenyl)carbamate did not contain herbicidal residues in excess of 0.05 p.p.m. which is the low sensitivity limit of the method.

THE BIOLOGICAL ACTIVITY of isopropyl N-phenylcarbamate (IPC) and isopropyl N-(3-chlorophenyl)carbamate (CIPC) as selective weed control agents applied to agricultural crops has been studied extensively at universities and experiment stations throughout the country. It was necessary to analyze the treated crops to determine whether any residues of the herbicides remained at harvest. Through the cooperation of the above agencies, samples of treated and untreated crops were harvested without delay and shipped to the Barberton Laboratory of Columbia-Southern Chemical Corp., where the residue analyses were conducted.

Residue analyses were made of certain agricultural food crops, which were treated at some stage during growth or maturity with either CIPC or IPC.

A method for determining micro amounts of IPC in lettuce, reported by Bissinger and Fredenburg (1), served as the basis of a method proposed by Gard and Rudd (3) for determining trace amounts of CIPC in crops and soils. In 1954, Gard, Pray, and Rudd (2) pre-

sented residue analyses of selected crops grown in treated soil, which included head lettuce, sugar beets (roots and foliage), onions, cotton seeds, peanuts, and spinach. These analyses indicated net residue values ranging between 0.00 and 0.03 p.p.m. of CIPC, which were actually below the low sensitivity level of detection by the method. The present work extends application of the Gard-Rudd method to grapes, tomatoes, carrots, sweet potatoes, strawberries, and peaches. Also, analyses are presented which demonstrate application of the method to IPC residues in shelled peas.

The analytical method (3) was shown previously to have an average recovery of 90% when the herbicide was added in the range of 0.05 to 0.5 p.p.m. of CIPC and a precision, based on 95% confidence limits, determined by statistical methods, of ±0.016 p.p.m. of CIPC. Present experiments in the testing of additional crops sustain this degree of recovery.

Table I. Recovery of Isopropyl N-Phenylcarbamate from Peas

IPC Added		Red Light Transmittance,	IPC Found			
			Total		Net	
Mg.	P.p.m.	%	Mg.	P.p.m.	P.p.m.[a]	% recovery
0.000	0.000	81	0.0078	0.039	. . .	. . .
0.000	0.000	85	0.0020	0.010	. . .	. . .
0.000	0.000	83	0.0038	0.019	. . .	. . .
0.010	0.050	74	0.0168	0.084	0.061	122
0.010	0.050	77	0.0130	0.065	0.042	84
0.020	0.100	68	0.0244	0.122	0.099	99
0.020	0.100	65	0.0302	0.151	0.128	128
0.030	0.150	68	0.0244	0.122	0.099	66

[a] Net recovery calculated after deducting an average correction of 0.023 p.p.m. due to interference found in untreated crop.