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*) presented 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.

Table II. Recovery of Isopropyl *N*-(3-Chlorophenyl)carbamate from Food Crops

CIPC Added		Red Light Transmittance,	CIPC Found			
			Total		Net	
Mg.	P.p.m.	%	Mg.	P.p.m.	P.p.m.[a]	% recovery
Grapes						
0.000	0.000	80	0.0076	0.038	...	...
0.000	0.000	79	0.0084	0.042	...	...
0.000	0.000	87	0.0000	0.000	...	...
0.010	0.050	75	0.0134	0.067	0.040	80
0.010	0.050	75	0.0134	0.067	0.040	80
0.015	0.075	71	0.0174	0.087	0.060	80
0.020	0.100	63	0.0294	0.147	0.120	120
0.020	0.100	68	0.0214	0.107	0.080	80
Tomatoes						
0.000	0.000	87	0.0000	0.000	...	...
0.000	0.000	89	0.0000	0.000	...	...
0.000	0.000	88	0.0000	0.000	...	...
0.010	0.050	76	0.0116	0.058	0.058	116
0.010	0.050	78	0.0100	0.050	0.050	100
0.020	0.100	72	0.0168	0.084	0.084	84
0.020	0.100	68	0.0218	0.109	0.109	109
0.030	0.150	65	0.0268	0.134	0.134	89
Carrots						
0.000	0.000	87	0.0000	0.000	...	...
0.000	0.000	85	0.0016	0.008	...	...
0.000	0.000	87	0.0000	0.000	...	...
0.010	0.050	77	0.0102	0.051	0.048	96
0.010	0.050	77	0.0102	0.051	0.048	96
0.020	0.100	72	0.0162	0.081	0.078	78
0.020	0.100	75	0.0136	0.068	0.065	65
0.030	0.150	68	0.0212	0.106	0.103	69
Sweet potatoes						
0.000	0.000	83	0.0034	0.017	...	...
0.000	0.000	87	0.0000	0.000	...	...
0.000	0.000	87	0.0000	0.000	...	...
0.010	0.050	78	0.0092	0.046	0.040	80
0.010	0.050	78	0.0092	0.046	0.040	80
0.020	0.100	71	0.0172	0.086	0.080	80
0.020	0.100	73	0.0152	0.076	0.070	70
0.030	0.150	61	0.0312	0.156	0.150	100
Strawberries						
0.000	0.000	77	0.0107	0.053	...	...
0.000	0.000	77	0.0107	0.053	...	...
0.000	0.000	76	0.0118	0.059	...	...
0.010	0.050	70	0.0194	0.097	0.042	84
0.010	0.050	70	0.0194	0.097	0.042	84
0.010	0.050	69	0.0205	0.103	0.048	96
0.010	0.050	69	0.0205	0.103	0.048	96
0.010	0.050	69	0.0205	0.103	0.048	96
Peaches						
0.000	0.000	80	0.0075	0.038	...	...
0.000	0.000	80	0.0075	0.038	...	...
0.000	0.000	79	0.0084	0.042	...	...
0.010	0.050	72	0.0167	0.084	0.045	90
0.010	0.050	72	0.0167	0.084	0.045	90
0.010	0.050	73	0.0157	0.079	0.040	80
0.010	0.050	73	0.0157	0.079	0.040	80
0.010	0.050	73	0.0157	0.079	0.040	80

[a] Following corrections due to interferences found in untreated crops were deducted from total residues in order to obtain net residues: grapes, 0.027; tomatoes, 0.000; carrots, 0.003; sweet potatoes, 0.006; strawberries, 0.055; and peaches, 0.039 p.p.m.

Source and Treatment of Crops

The herbicidal application to crops is given in the following list.

Grapes. The soil beneath the grapevines was treated by spraying in the spring of the year over a 3-year period prior to the initiation of growth of the grape plant and prior to the germination of most weeds in the vineyard. An emulsifiable form of CIPC was applied in 24-inch bands beneath the grape trellis. Ten pounds of CIPC in 50 gallons of water per acre was applied the first year and 14 pounds in 50 gallons of water was applied during the following 2 consecutive years.

Tomatoes. The tomato plants were treated by spraying at "lay-by" with 2 and 4 pounds, respectively, of CIPC in 50 gallons of water per acre. One sample of tomatoes was from plants treated at lay-by with 2 pounds of CIPC in dry form impregnated on 50 pounds of 30 to 60 mesh Attaclay per acre. After application, any granules adhering to the plants were brushed off.

Peas. The soil was treated by spraying an emulsifiable form of IPC to the soil and working it into the soil to a depth of about 4 inches prior to planting. Applications were made at the rate of 4 and 16 pounds, respectively, of IPC in 40 gallons of water per acre.

Carrots. The carrots were treated by spraying the plants during the cotyledon stage with 4 pounds of CIPC in 50 gallons of Stoddard solvent per acre.

Sweet Potatoes. The sweet potato vines were treated by spraying when the vines were 2 to 3 feet long at "lay-by." The spray was applied at the rate of 2 pounds of CIPC in 50 gallons of water per acre.

Strawberries. The strawberry plants were treated by spraying at the onset of dormancy in the fall of the year prior to harvest. The spray was applied at the rate of 3 pounds of CIPC in 50 gallons of water per acre.

Peaches. The peach trees were treated by spraying with CIPC as a chemical thinning agent for the bloom, in the spring when about 80% of the shucks were off. The spray was an emulsion containing 500 p.p.m. of CIPC and was applied at the rate of 2 gallons per tree.

All perishable crops were transported under conditions necessary for preservation of the crops, and, on arrival at the laboratory, were stored in the refrigerator at 20° F. to preserve the crop and minimize any loss of the herbicide by volatilization until actual testing could be commenced.

Interferences with Analytical Method

Application of the method for determining CIPC and IPC residues in crops showed varying amounts of an unknown material (*2*, *3*) which caused interference by producing very slight blue colors in the colorimetric method. The interference was subtracted from the gross amount of the herbicides found in the treated crops.

Analytical Method

Investigation showed that IPC responded quantitatively in a manner similar to CIPC when subjected to the analytical method described. In fact, the photoelectric transmittance per unit of concentration of these two carbamates was virtually identical, which simplified technical operations when the two herbicides were involved in the crop analysis. The data given in Table I show typical analyses of the untreated peas and recovery of IPC. In Table II, data for other crops show typical analyses of untreated samples, and the recovery of CIPC obtained by the test method.

The method of Gard and Rudd (2, 3) was applied to both herbicides to form 3-chloroaniline in the case of CIPC or aniline in the case of IPC. Colorimetric measurement by the phenol-hypochlorite method (4) was made utilizing a photoelectric colorimeter equipped with 5-cm. comparison cells and a red light filter (650 mμ).

A very careful evaluation of the reagent blank was necessary in the recovery and crop analyses at extremely low concentration levels.

Experiments showed that the transmittance readings for the reagent blank involving no crops and varying lots of reagents ranged between 87 and 93%, as compared with distilled water, and were dependent on the purity of the particular lots of reagents used. Each new lot of reagents, therefore, required careful evaluation prior to use in order to establish the origin of the calibration curve. For convenience of comparing the transmittance data from the various crops, all such values listed in Tables I and II are computed on the basis of 87% transmittance as the zero point because it was at this value that most of the reagent-blank tests fell. The precision of this blank for given lots of reagents was ±1% transmittance.

Table III. Isopropyl *N*-(3-Chlorophenyl)carbamate Residue in Crops Receiving Treatment

Crops	Treatment, Lb. CIPC/Acre	CIPC Found, P.P.M. — Replicate Tests 1	2	3	4	5	Av.	Net
Grapes	None	0.04	0.04	0.00	0.02	0.03	0.026	...
	10-14-14[a]	0.03	0.03	0.01	0.02	0.02	0.022	−0.004
Tomatoes	None	0.00	0.00	0.00	0.00	0.00	0.000	...
	2[b]	0.00	0.03	0.02	0.04	0.03	0.024	0.024
	4[b]	0.03	0.00	0.00	0.01	0.01	0.010	0.010
	2[c]	0.02	0.00	0.00	0.00	0.01	0.006	0.006
Carrots	None	0.00	0.01	0.00	0.01	0.00	0.004	...
	4[b]	0.06	0.04	0.05	0.06	0.04	0.050	0.046
Sweet potatoes	None	0.02	0.00	0.00	0.00	0.00	0.003	...
	2[b]	0.03	0.01	0.01	0.01	0.01	0.014	0.011
Strawberries	None	0.05	0.05	0.06	0.06	0.05	0.054	...
	3[b]	0.05	0.05	0.05	0.04	0.05	0.048	−0.006
Peaches	None	0.04	0.04	0.04	0.04	0.04	0.040	...
	[d]	0.04	0.03	0.04	0.04	0.02	0.034	−0.006

[a] Spraying during three successive years prior to harvest.
[b] Spray application.
[c] Pellet application.
[d] Spraying at rate of 2 gal. of 500 p.p.m. of CIPC per tree.

Table IV. Isopropyl *N*-Phenylcarbamate Residue in Peas Receiving Treatment

Treatment, Lb. IPC/Acre	IPC Found, P.P.M. — Replicate Tests 1	2	3	4	5	Av.	Net
None	0.04	0.01	0.02	0.04	0.01	0.024	...
4	0.02	0.00	0.00	0.00	0.00	0.004	−0.020
14	0.05	0.02	0.00	0.00	0.00	0.014	−0.010

Analytical Results

The results of replicate testing of the crops utilizing 200-gram specimens are given in Tables III and IV. To obtain the apparent net amount of CIPC residue which remained with the treated crops at harvest, the control analyses represented by crops receiving no treatment were subtracted from the values obtained with crops receiving the various levels of herbicidal treatment. In some cases the control analyses are slightly larger than the values for treated crops, which indicates the uncertainty of the presence of any of the herbicides. In any event, the net analyses are considerably below the practical limit of identification of the method in all cases excepting the treated carrot crop, where the net analysis is only slightly below the 0.05-p.p.m. level. In interpreting the residue analysis it is recognized that the herbicides may have become detoxified or otherwise assimilated and metabolized during growth of the plant or fruit and therefore may not be detected as such by the analytical method.

Summary

The CIPC and IPC residues found at harvest in the crops receiving treatment, after correction for interference, ranged from apparent slightly negative residue values in the cases of grapes, strawberries, peaches, and peas to a maximum of 0.05 p.p.m. of CIPC in the case of carrots. It is conceivable that radioisotope techniques may be more applicable to the determination at hand than the strictly chemical methods thus far investigated.

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