graphically illustrated in Figures 2 and 4, is not surprising, because Frankenburg found it among the products from the fermentation of tobacco, from the irradiation of nicotine with ultraviolet light, and from the autoxidation of nicotine (*12*). Recently, McKennis, Turnbull, Wingfield, and Dewey (*19*) found cotinine as a metabolic product of nicotine in mammals, and Guthrie, Ringler, and Bowery (*15*) reported cotinine as a metabolite of nicotine in insects.

Quantitative recovery from the plant tissues of any of the compounds mentioned is not claimed, and it is probable that differential losses of constituents occurred during the many partitioning steps utilized. In these procedures, for example, manipulative losses would be expected to involve nornicotine > anabasine > nicotine. Nicotinic acid was not included among the candidate degradation products.

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**HERBICIDE RESIDUES**

# Effect of Higher Application Rates on Crop Residues of Isopropyl *N*-Phenylcarbamate and Isopropyl *N*-(3-Chlorophenyl)carbamate

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**The expanding experimental use of isopropyl *N*-(3-chlorophenyl)carbamate and isopropyl *N*-phenylcarbamate as selective herbicides has created the need for further residue studies on a number of new crops. Residue analyses are reported for rice, celery, peas, pea forage, lima beans, green beans, soybeans, and soybean forage receiving treatment with CIPC. Residue analyses are also given for spinach, strawberries, and sugar beets treated with IPC. The analytical method of Gard and Rudd for determining micro quantities of CIPC in crops was successfully used for the measurement of both carbamate residues. Some of these crops received greater than normal treatment and no residue was found which exceeded 0.05 p.p.m., the lower limit of sensitivity of the analytical method.**

Over the past several years the increasing experimental use of isopropyl *N*-phenylcarbamate (IPC) and isopropyl *N*-(3-chlorophenyl)carbamate (CIPC) as selective herbicides has emphasized the effectiveness of these compounds in controlling grasses and narrow-leaf weeds during the growth of edible food crops such as rice, celery, grapes, tomatoes, carrots, sweet potatoes, onions, spinach, strawberries, lettuce, peanuts, cottonseeds, peas, and sugar beets.

Smith's (*5*) results with rice crops showed that the average yield of harvested rice increased from about 56 to about 100 bushels of rice per acre when one technique was used for applying the CIPC, and from about 34 to about 86 bushels per acre in another experiment using another mode of application.

Residue analyses (*1, 2*) have shown that any residues remaining with the crops treated at recommended rates are below the sensitivity limits of the method—i.e., 0.05 p.p.m. of CIPC and IPC. As experimental use of these herbicides is extended to other crop applications it is very important, from a toxicological viewpoint, to determine any residues which remain at harvest.

Recently the U. S. Department of Agriculture requested that residue analyses be conducted on crops grown in soil treated with CIPC at two to three times the normally recommended application rate, to simulate conditions which might prevail when crops are planted in soils treated with the herbicide earlier in the season, or when the herbicide is applied at higher than recommended rates. Results are given for several such crops grown in soil under these conditions. In addition, residue data not previously reported for other crops receiving the recommended treatment rate of IPC and CIPC are given.

### Treatment of Crops

**Peas, Pea Forage, Lima Beans, Soybeans, and Green Beans.** Pre-emergence treatment was by spraying an emulsifiable form of CIPC at the time of planting. The crops, except soybeans, were treated at the rate of 10 pounds per acre. The soybeans received 14 pounds per acre.

**Rough Rice.** Pre-emergence treatment was by spraying an emulsifiable form of CIPC at a rate of 6 pounds per acre.

**Celery.** Two lots of celery were examined, which involved different treatment procedures with CIPC. The first lot was treated by spraying the herbicide in Stoddard solvent at the rate of 4 pounds per acre after transplanting the plants. The second lot was treated by spraying an emulsifiable form of CIPC in water at a rate of 10 pounds per acre prior to transplanting the plants.

**Strawberries.** Treatment was conducted during the dormant period of the plants by spraying an emulsifiable concentrate of IPC at the rate of 6 pounds per acre.

**Sugar Beets.** This crop comprised comparatively small samples receiving pre-emergence treatments, by spraying an emulsifiable form of IPC at rates ranging from 2.5 to 4.6 pounds per acre. A composite sample of this crop was prepared, which gave an average treatment of 3.2 pounds of the herbicide per acre.

**Spinach.** Pre-emergence treatment was conducted with IPC by spraying an emulsion containing 8 pounds in 60 gallons of water per acre. The crop subjected to postemergence treatment involved the use of 4 pounds of IPC in 60 gallons of water per acre.

### Analytical Method

To determine the amount of the two herbicides, IPC and CIPC, remaining as a residue in the treated food crops, the analytical method of Gard and Rudd (*3*) for determining micro quantities of CIPC was successfully used for the measurement of both carbamate residues. This method entails maceration of 200-gram samples of the crop with a solvent in a Waring Blendor. After thorough blending, the extract is separated from the pulp by centrifuging or filtering. The extract is then concentrated by evaporating the solvent, and the herbicide residue is hydrolyzed by refluxing gently with dilute sulfuric acid to convert any IPC or CIPC to aniline or 3-chloroaniline.

The resulting aniline is then steam-distilled from the solution, after being rendered alkaline with an excess of sodium hydroxide. The distillate is treated with 5% calcium hypochlorite solution, and after reaction for 2 minutes,

**Table I. 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. | Recovery, % |
| | | | Rough Rice | | | |
| 0.000 | 0.000 | 94 | 0.0000 | 0.000 | ... | .. |
| | | 93 | 0.0013 | 0.007 | ... | .. |
| | | 91 | 0.0032 | 0.016 | ... | .. |
| 0.010 | 0.050 | 80 | 0.0146 | 0.073 | 0.065 | 130 |
| | | 83 | 0.0115 | 0.058 | 0.050 | 100 |
| | | 80 | 0.0146 | 0.073 | 0.065 | 130 |
| 0.020 | 0.100 | 77 | 0.0184 | 0.092 | 0.084 | 84 |
| | | 76 | 0.0192 | 0.096 | 0.088 | 88 |
| | | | Celery | | | |
| 0.000 | 0.000 | 92 | 0.0022 | 0.011 | ... | .. |
| | | 94 | 0.0000 | 0.000 | ... | .. |
| | | 94 | 0.0000 | 0.000 | ... | .. |
| 0.010 | 0.050 | 83 | 0.0115 | 0.058 | 0.055 | 110 |
| | | 80 | 0.0146 | 0.073 | 0.065 | 130 |
| | | 80 | 0.0146 | 0.073 | 0.065 | 130 |
| 0.020 | 0.100 | 78 | 0.0170 | 0.085 | 0.082 | 82 |
| 0.030 | | 75 | 0.0202 | 0.101 | 0.098 | 65 |
| | | | Peas, Shelled | | | |
| 0.000 | 0.000 | 93 | 0.0013 | 0.007 | ... | .. |
| | | 89 | 0.0053 | 0.027 | ... | .. |
| | | 89 | 0.0053 | 0.027 | ... | .. |
| 0.010 | 0.050 | 76 | 0.0192 | 0.096 | 0.076 | 152 |
| | | 84 | 0.0104 | 0.052 | 0.032 | 64 |
| | | 78 | 0.0170 | 0.085 | 0.065 | 130 |
| 0.020 | 0.100 | 69 | 0.0284 | 0.142 | 0.122 | 122 |
| | | 67 | 0.0316 | 0.158 | 0.138 | 138 |
| | | | Peas, Forage | | | |
| 0.000 | 0.000 | 93 | 0.0013 | 0.007 | ... | .. |
| | | 94 | 0.0000 | 0.000 | ... | .. |
| | | 87 | 0.0068 | 0.034 | ... | .. |
| 0.010 | 0.050 | 83 | 0.0115 | 0.058 | 0.044 | 88 |
| | | 80 | 0.0146 | 0.073 | 0.059 | 118 |
| | | 81 | 0.0137 | 0.069 | 0.055 | 110 |
| 0.020 | 0.100 | 77 | 0.0184 | 0.092 | 0.078 | 78 |
| | | 77 | 0.0184 | 0.092 | 0.078 | 78 |
| | | | Green Beans | | | |
| 0.000 | 0.000 | 93 | 0.0013 | 0.007 | ... | .. |
| | | 93 | 0.0013 | 0.007 | ... | .. |
| | | 93 | 0.0013 | 0.007 | ... | .. |
| 0.010 | 0.050 | 85 | 0.0086 | 0.043 | 0.038 | 76 |
| | | 84 | 0.0104 | 0.052 | 0.045 | 90 |
| | | 85 | 0.0086 | 0.043 | 0.038 | 76 |
| 0.020 | 0.100 | 80 | 0.0146 | 0.073 | 0.066 | 66 |
| | | 71 | 0.0254 | 0.127 | 0.120 | 120 |
| | | | Lima Beans, Shelled | | | |
| 0.000 | 0.000 | 93 | 0.0013 | 0.007 | ... | .. |
| | | 94 | 0.0000 | 0.000 | ... | .. |
| | | 94 | 0.0000 | 0.000 | ... | .. |
| 0.010 | 0.050 | 84 | 0.0104 | 0.052 | 0.049 | 98 |
| | | 84 | 0.0104 | 0.052 | 0.049 | 98 |
| | | 85 | 0.0086 | 0.043 | 0.040 | 80 |
| 0.020 | 0.100 | 77 | 0.0184 | 0.092 | 0.089 | 89 |
| | | 74 | 0.0220 | 0.110 | 0.107 | 107 |

a 5% solution of phenol in 5% ammonia is added to produce the blue complex. This color is then measured with a suitable photoelectric colorimeter or spectrophotometer. The amount of IPC or CIPC found in the sample is then determined from a previously prepared calibration curve.

As analyses of the various crops progressed, it was found that making various modifications in the method facilitated its application to specific crops and generally improved its over-all performance. For example, in some cases the nature of the crop made it advisable to use methanol or ethyl alcohol as the extracting solvent, instead of the methylene dichloride called for in the original analytical method.

The method directing the use of methylene dichloride as an extracting solvent was applied directly to the shelled peas without undue difficulty. However, attempts to analyze the pea forage crop, using the methylene dichloride solvent, simultaneously extracted large quantities of unknown materials from the leaves and stems, which interfered with the recovery of extremely low amounts of herbicide from the forage crop. The use of methanol as extractant with subsequent re-extraction of the methanol solution with petroleum ether eliminated considerable amounts of interferences, improved the accuracy as well as the precision of the recovery analyses, and reduced the value of the blank or control as interference necessarily subtracted from recovery samples and treated crops.

A similar problem arose on analyzing the green beans, although not to such an extent as with the pea forage. Again the use of methanol as extractant improved the performance of the basic analytical method.

Early in the experimental work with these crops it was noted that during the steam distillation step, when the hydrolyzed IPC or CIPC was distilled as aniline or 3-chloroaniline, varying amounts of oils were also steam distilled. As these oils cause turbidity in the final solution, interfering with colorimetric measurements, Gard recommended filtering the distillate through double thicknesses of filter paper before the hypochlorite addition step. This filtration was not found to be completely successful in eliminating the turbidity in every case. To resolve this problem a small amount of Celite was added to the distillate and stirred, and then filtered before reaction with the hypochlorite. This treatment in every case completely clarified the solution and eliminated the turbidity caused by the steam-distilled oils.

These modifications illustrate how the basic method can be adapted and made applicable to many different types of crops. The data given in Table I show typical analyses of the untreated crops listed and the recovery of CIPC. In Table II, similar analyses and recovery data are given for IPC.

**Table II. Recovery of Isopropyl *N*-Phenylcarbamate from Food Crops**

| IPC Added | | Red Light Transmittance, | IPC Found | | | |
|---|---|---|---|---|---|---|
| | | | Total | | Net | |
| Mg. | P.p.m. | % | Mg. | P.p.m. | P.p.m. | Recovery, % |
| | | | Strawberries | | | |
| 0.000 | 0.000 | 87 | 0.0079 | 0.040 | ... | .. |
| | | 90 | 0.0048 | 0.024 | ... | .. |
| | | 88 | 0.0073 | 0.037 | ... | .. |
| 0.010 | 0.050 | 79 | 0.0186 | 0.093 | 0.059 | 118 |
| | | 80 | 0.0174 | 0.087 | 0.053 | 106 |
| 0.020 | 0.100 | 75 | 0.0236 | 0.118 | 0.084 | 84 |
| | | 76 | 0.0222 | 0.111 | 0.077 | 77 |
| 0.030 | 0.150 | 75 | 0.0236 | 0.118 | 0.084 | 56 |
| | | | Sugar Beets, Roots | | | |
| 0.000 | 0.000 | 94 | 0.0000 | 0.000 | ... | .. |
| | | 93 | 0.0014 | 0.007 | ... | .. |
| | | 93 | 0.0014 | 0.007 | ... | .. |
| 0.010 | 0.050 | 81 | 0.0152 | 0.076 | 0.071 | 144 |
| | | 81 | 0.0152 | 0.076 | 0.071 | 144 |
| | | 84 | 0.0116 | 0.058 | 0.053 | 106 |
| 0.020 | 0.100 | 75 | 0.0236 | 0.118 | 0.113 | 113 |
| | | 74 | 0.0246 | 0.123 | 0.118 | 118 |
| | | | Sugar Beets, Foliage | | | |
| 0.000 | 0.000 | 93 | 0.0014 | 0.007 | ... | .. |
| | | 93 | 0.0014 | 0.007 | ... | .. |
| | | 95 | 0.0000 | 0.000 | ... | .. |
| 0.010 | 0.050 | 84 | 0.0118 | 0.059 | 0.054 | 108 |
| | | 84 | 0.0118 | 0.059 | 0.054 | 108 |
| | | 82 | 0.0145 | 0.071 | 0.066 | 132 |
| 0.020 | 0.100 | 83 | 0.0130 | 0.065 | 0.060 | 60 |
| | | 76 | 0.0222 | 0.112 | 0.107 | 107 |
| | | | Spinach | | | |
| 0.000 | 0.000 | 94 | 0.0000 | 0.000 | ... | .. |
| | | 93 | 0.0014 | 0.007 | ... | .. |
| | | 91 | 0.0029 | 0.015 | ... | .. |
| 0.010 | 0.050 | 84 | 0.0116 | 0.058 | 0.051 | 102 |
| | | 86 | 0.0096 | 0.048 | 0.041 | 82 |
| | | 87 | 0.0079 | 0.040 | 0.033 | 66 |
| 0.020 | 0.100 | 76 | 0.0222 | 0.111 | 0.104 | 104 |
| | | 75 | 0.0236 | 0.118 | 0.111 | 111 |

In applying the method to these crops, a very careful evaluation of the reagent blank was necessary before the recovery and crop analyses, because of the extremely low concentration levels of residue expected. Experiments showed that the photoelectric transmittance readings for the reagent blank involving no crops, but with varying lots of reagents ranged from 87 to 94%, 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 re-evaluation of the reagent blank prior to use in order to establish the origin of the calibration curve.

All analytical values listed in Tables I and II, except transmittance results, were computed from transmittance curves based on the blank obtained for the reagents used for each crop. For ease of comparison, the transmittance results were corrected to the value they would have been, if the reagent blank had been 94% in each case. The precision of the reagent blank tests for given lots of reagents was ±1% transmittance.

### Analytical Results

The results of replicate tests of the crops utilizing 200-gram portions o sample are given in Tables III and IV The crops listed in Table III, which received treatment at 10 pounds of CIPC per acre, are those subjected to two to three times the recommended rate of herbicidal treatment.

To obtain the apparent net amount of CIPC and IPC residue which remained with the treated crops at harvest, the results of the control analyses, represented by crops receiving no treatment, were subtracted from the values obtained for crops receiving the various levels of herbicidal treatment. In all cases, the net residues found are considerably below the practical limit of identification of the method, which is 0.05 p.p.m. of the herbicide.

In addition to the crops listed in Tables I and III, soybeans also received the higher than normal application rate, and analyses of both the dried soybeans and the complete soybean forage consisting of beans, pods, leaves, stems, and vines were attempted. In the case of the dried soybeans the oil extracted by the solvents contained unknown compounds which interfered with the hydrolysis and distillation of the CIPC. An attempt was made to separate the herbicide from the oil, by extracting the oil with acetonitrile, as suggested in the basic analytical method (*3*) and found applicable to peanuts and cottonseed. However, even with the most careful work there remained in the acetonitrile layer interfering substances of an undetermined nature extracted from the soybean oil which responded to the test for CIPC and gave large interference values for the control crop of beans. A number of other variations in the extracting and separating stages were attempted without reducing the amount of the interference to a level where satisfactory values could be obtained for recovery analyses and treated crop analyses. The same difficulties arose during the analysis of the soybean forage.

By way of illustrating this difficulty, control tests of untreated samples of dried soybeans gave transmission values ranging from 75 to 85%, the average of 13 analyses being 82%. From the calibration curve used in these analyses, these values represent between 0.0092 and 0.0194 mg. of CIPC or between 0.043 and 0.101 p.p.m. as CIPC, the average value being 0.0124 mg. or 0.062 p.p.m. of CIPC. Similar data were obtained in analyzing samples of soybean forage which had received no CIPC treatment. These results show that attempts to report concentration values in the range of 0.05 p.p.m. or less in the presence of such large blank values cannot be justified analytically.

Nevertheless, analyses performed on control samples, recovery samples, and on portions of the treated crops of dried soybeans and forage indicated that residue in the treated soybean crop was in approximately the same concentration range as the other treated crops.

A greater residue of herbicide may not necessarily be found in crops treated at higher application rates. Natural disappearance of the herbicide from soil—i.e., by microbial decomposition, leaching, adsorption by soil colloids, and volatilization (*4*)—may account for the low residues in these crops. The herbicides absorbed by the plants themselves may be assimilated or metabolized during growth and maturity of the plant and may not be detected as such by this analytical method.

**Table III. Isopropyl *N*-(3-Chlorophenyl)carbamate Residues**

| Treatment, Lb. CIPC/Acre | CIPC Found, P.P.M. — Replicate Tests 1 | 2 | 3 | 4 | 5 | Av. | Net |
|---|---|---|---|---|---|---|---|
| | | | Rough Rice | | | | |
| None | 0.00 | 0.01 | 0.02 | 0.00 | 0.01 | 0.008 | ... |
| 6[a] | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.014 | 0.006 |
| | | | Celery | | | | |
| None | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.002 | ... |
| 4[b] | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.014 | 0.012 |
| 10[c,d] | 0.05 | 0.02 | 0.00 | 0.01 | 0.00 | 0.016 | 0.014 |
| | | | Peas, Shelled | | | | |
| None | 0.01 | 0.03 | 0.03 | 0.06 | 0.02 | 0.030 | ... |
| 10[a,d] | 0.03 | 0.02 | 0.02 | 0.01 | 0.06 | 0.028 | −0.002 |
| | | | Peas, Forage | | | | |
| None | 0.01 | 0.00 | 0.03 | 0.01 | 0.03 | 0.016 | ... |
| 10[a,d] | 0.06 | 0.03 | 0.03 | 0.03 | 0.03 | 0.036 | 0.020 |
| | | | Green Beans | | | | |
| None | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.006 | ... |
| 10[a] | 0.03 | 0.02 | 0.04 | 0.02 | 0.06 | 0.034 | 0.028 |
| | | | Lima Beans, Shelled | | | | |
| None | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.004 | ... |
| 10[a,d] | 0.03 | 0.04 | 0.03 | 0.02 | 0.01 | 0.026 | 0.022 |

[a] Pre-emergence treatment by spraying. [b] Spray treatment after transplanting. [c] Spray treatment prior to transplanting. [d] Treated at 2–3 times recommended rate.

**Table IV. Isopropyl *N*-Phenylcarbamate Residues**

| Treatment, Lb. IPC/Acre | IPC Found, P.P.M. — Replicate Tests 1 | 2 | 3 | 4 | 5 | Av. | Net |
|---|---|---|---|---|---|---|---|
| | | | Strawberries | | | | |
| None | 0.04 | 0.02 | 0.04 | 0.03 | 0.04 | 0.034 | ... |
| 6[a] | 0.02 | 0.02 | 0.01 | 0.00 | 0.03 | 0.016 | −0.018 |
| | | | Sugar Beets, Roots | | | | |
| None | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.006 | ... |
| 3.2[b] | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.008 | 0.002 |
| | | | Sugar Beets, Foliage | | | | |
| None | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.004 | ... |
| 3.2[b] | 0.04 | 0.01 | 0.01 | 0.01 | 0.01 | 0.016 | 0.012 |
| | | | Spinach | | | | |
| None | 0.00 | 0.01 | 0.02 | 0.00 | 0.00 | 0.006 | ... |
| 4[c] | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.008 | 0.002 |
| 8[b] | 0.03 | 0.03 | 0.01 | 0.01 | 0.02 | 0.020 | 0.014 |

[a] Spray treatment during dormancy of plant prior to production of berries. [b] Pre-emergence treatment by spraying. [c] Postemergence treatment by spraying.

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