

**Endosulfan Residues on Treated Crops.** Chard, lettuce, and table beets received two spray applications of endosulfan at the rate of 1 pound per acre. Collards and turnip greens were sprayed four times with 0.75 pound of technical endosulfan per acre. One plot of sugar beets was treated about 6 months before harvest with a granular formulation at

the rate of 1 pound of technical endosulfan per acre. A second plot was treated in the same manner, then treated a second time 1 month later. The residues found are given in Table III.

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## INSECTICIDE RESIDUES

# Determination of Residual 4-Dimethylamino-3,5-xylol Methylcarbamate and 4-Dimethylamino-3,5-xylol by Use of Luteoarsenotungstic Acid

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Procedures for the residue determinations of 4-dimethylamino-3,5-xylol methylcarbamate ("carbamate") and 4-dimethylamino-3,5-xylol ("xylol") in peaches and undelinted cottonseed are given. The "xylol" is determined colorimetrically with a highly specific reagent, luteoarsenotungstic acid; the "xylol" produced by the saponification of 4-dimethylamino-3,5-xylol methylcarbamate is determined as a measure of the "carbamate."

**Z**ECTRAN (registered trademark of The Dow Chemical Co.) insecticide, containing the active ingredient 4-dimethylamino-3,5-xylol methylcarbamate, has proved useful on deciduous fruits and other edible products. It has also been used in the treatment of cottonseed and ornamental plants. Thus analytical methods for residual amounts of this chemical in a variety of media were needed.

The methods given account for the analysis of residual quantities of the active ingredient as well as the hydrolytic product, 4-dimethylamino-3,5-xylol, in two typical crops, peaches and cottonseed. The usual procedure for this type of carbamate ester is to determine colorimetrically the phenol derivative produced by its saponification. Determination of the 4-dimethylamino-3,5-xylol before and after saponification would thus distinguish between the two compounds.

However, most of the usual colorimetric methods for phenols do not work with 4-dimethylamino-3,5-xylol. Procedures using nitrous acid (4), diazotized *p*-nitroaniline (6), 2,6-dibromoquinone-chloroimide (2), or 4-aminoantipyrine (3) fail to give a color reaction or lack sensitivity.

Phosphotungstomolybdic acid, as in the phenol reagent of Folin and Cioccoltin (7), gives a sensitive color test with 4-dimethylamino-3,5-xylol; however, it likewise gives a color with the carbamate ester. Furthermore, since this reagent is

very sensitive to reducing agents, excessive cleanup of the pesticide from agricultural products is necessary to obtain acceptable blanks.

Luteoarsenotungstic acid [ $H_6(18WO_3 \cdot As_2O_8)$ ] (5) gives a blue color with 4-dimethylamino-3,5-xylol but does not give any color with 4-dimethylamino-3,5-xylol methylcarbamate. In addition, the luteoarsenotungstic acid has a high degree of specificity for this phenol because *o*-aminophenol and *p*-aminophenol and their derivatives are the only monophenols that give a positive test with this reagent, although polyphenols will give a blue color. Since the reagent is insensitive to mild reducing agents, cleanup of the carbamate pesticide and its hydrolytic product from agricultural products in order to obtain low blanks is relatively easy.

By using the ideal properties of luteoarsenotungstic acid as a colorimetric reagent, the following procedures for the residue determinations of 4-dimethylamino-3,5-xylol and 4-dimethylamino-3,5-xylol methylcarbamate were developed.

#### Colorimetric Procedures

**Reagents.** Sulfuric acid, approximately 6*N* stock solution. Cautiously add 168 ml. of concentrated sulfuric acid (95.5%) to about 750 ml. of water. Cool the aqueous solution to room temperature and dilute it to 1 liter.

Dilute 1 volume of 6*N* sulfuric acid to 3 volumes with water to obtain approximately 2*N* sulfuric acid.

Potassium hydroxide, approximately 2.5*N*. Dissolve 165 grams of 85% potassium hydroxide pellets in about 750 ml. of water. Cool the solution, dilute to 1000 ml., and keep in a polyethylene bottle.

Luteoarsenotungstic acid reagent (5). Add 200 ml. of water to 50 grams of arsenic pentoxide and 20 grams of sodium tungstate,  $Na_2WO_4 \cdot 2H_2O$ , in a 500-ml., round-bottomed flask. Reflux the mixture for 1½ hours. Pour the solution into a 400-ml. beaker; add 50 grams of lithium sulfate,  $Li_2SO_4 \cdot H_2O$ , and 5 or 6 drops of bromine. Boil the solution for 8 to 10 minutes to remove the excess bromine. Cool the solution, dilute to 250 ml. with water, and filter. Keep the reagent in a glass-stoppered amber bottle. The reagent is stable for at least 2 months and probably indefinitely.

Sodium carbonate, approximately 15% solution. Dissolve 150 grams of ACS-grade sodium carbonate in about 750 ml. of water and dilute the solution to 1000 ml.

4-Dimethylamino-3,5-xylol, m.p. 93.5–95° C.

4-Dimethylamino-3,5-xylol methylcarbamate, m.p. 85° C.

The last two chemicals may be obtained from Bioproducts Department, The Dow Chemical Co.

**Apparatus.** Coleman spectropho-

**Table I. Recovery of 4-Dimethylamino-3,5-xyleneol in Peaches**

Added, P.P.M.	Found, P.P.M.	Recovery, %
0.10	0.076	76
	0.081	81
0.20	0.166	83
	0.166	83
0.50	0.439	88
	0.435	87
1.00	0.856	86
	0.847	85
1.50	1.315	88
	1.315	88
2.00	1.844	92
	1.820	91
2.50	2.297	92
	2.344	94

tometer. Model 14, equipped with 4-cm. absorption cells. Any photometer measuring absorbance at 700 m $\mu$  should be suitable.

**Procedure for 4-Dimethylamino-3,5-xyleneol and Preparation of Standard Calibration Curve.** STANDARD SOLUTION 1. Dissolve 0.100 gram of 4-dimethylamino-3,5-xyleneol ("xyleneol") in 2*N* sulfuric acid and dilute the solution to 1 liter with 2*N* sulfuric acid. Concentration: 100  $\mu$ g. of the "xyleneol" per ml.

STANDARD SOLUTION 2. Dilute 25.0 ml. of standard solution 1 to 250 ml. with 2*N* sulfuric acid. Concentration: 10  $\mu$ g. of the "xyleneol" per ml.

STANDARD SOLUTION 3. Dilute 25.0 ml. of standard solution 2 to 250 ml. with 2*N* sulfuric acid. Concentration: 1  $\mu$ g. of the "xyleneol" per ml.

Using standard solutions 2 and 3, pipet 0, 4, 8, 20, 40, 60, 80, and 100  $\mu$ g. of the "xyleneol" into respective 250-ml. separatory funnels. Then add sufficient 2*N* sulfuric acid to make a total of 50 ml. of 2*N* sulfuric acid in each funnel. Proceed with the known amount of "xyleneol" in each funnel as follows: Wash the acid solution with three 25-ml. portions of chloroform (technical grade) and discard the washings. Neutralize the acid solution by cautiously adding 100 ml. of saturated sodium bicarbonate solution (USP-grade). Eliminate excess carbon dioxide by alternately shaking the neutralized solution and releasing the gas pressure. Extract the "xyleneol" from the aqueous solution with two 25-ml. portions of benzene (thiophene-free) and combine the extract solutions in a 125-ml. separatory funnel. Wash the solution with two 10-ml. portions of water and discard the washings.

Extract the "xyleneol" from the benzene solution with two 5.0-ml. portions of 0.5*N* sulfuric acid and combine the extract solutions in a 25-ml. volumetric flask. Pipet 1.0 ml. of luteoarsenotungstic acid reagent into the flask. Add 10 ml. of 15% sodium carbonate (add the first 4 ml. of the carbonate solution in 0.5-ml. increments and shake out

the carbon dioxide from the solution in the flask after the addition of each increment). Immediately dilute the solution to the mark with water and mix well. Five to 15 minutes after the addition of the sodium carbonate, fill a 4-cm. absorption cell with the solution and determine the absorbance with a spectrophotometer at 700 m $\mu$ , using water as a reference liquid. Prepare a standard calibration curve by plotting the data on graph paper. The curve prepared by the authors is shown in Figure 1.

**Procedure for 4-Dimethylamino-3,5-xylol Methylcarbamate and Preparation of Standard Calibration Curve.** Prepare standard solutions of 4-dimethylamino-3,5-xylol methylcarbamate ("carbamate") in 2*N* sulfuric acid in the same manner as described for "xyleneol." Pipet 0, 4, 8, 20, 40, 60, 80, 100, 120, and 140  $\mu$ g. of the "carbamate" into each of respective pairs of 250-ml. separatory funnels. Then add sufficient 2*N* sulfuric acid to make a total of 50 ml. of 2*N* sulfuric acid in each funnel. Proceed with the "carbamate" in each pair of separatory funnels as follows:

Wash each acid solution with three 25-ml. portions of chloroform and discard the washings. For the known amount of "carbamate" in one of the separatory funnels, continue the determination as in the procedure for 4-dimethylamino-3,5-xyleneol. For the same amount of "carbamate" in the other separatory funnel, add 50 ml. of 2.5*N* potassium hydroxide to the washed acid solution and mix well. After 2 or 3 minutes, add 20 ml. of 2*N* sulfuric acid and cool the separatory funnel and contents under cold tap water. Then add 25 ml. of saturated sodium bicarbonate solution and eliminate the excess carbon dioxide by alternately shaking the neutralized solution and releasing the gas pressure. Continue the determination as in the procedure for 4-dimethylamino-3,5-xyleneol.

Calculate the difference in absorbance obtained by the two procedures to get the net absorbance owing to the 4-dimethylamino-3,5-xylol methylcarbamate. Prepare a standard calibration curve by plotting the data on graph paper. The curve prepared by the authors is shown in Figure 1.

**Determination of 4-Dimethylamino-3,5-xyleneol and 4-Dimethylamino-3,5-xylol Methylcarbamate Residues in Peaches**

**Reagents.** Reagents already listed.

Filter aid. Hyflo Super-Cel, a Celite product, diatomaceous earth (Johns Manville Co.).

**Apparatus.** Meat grinder.

French-square bottle. Wide-mouthed, 500-ml., cap lined with polyethylene film.

Jar mill. Roller-type.

**Procedure for Determining 4-Di-**

**methylamino-3,5-xyleneol in Peaches.** Grind a sufficient quantity of treated whole peaches with a meat grinder. Weigh 100 grams of ground peach in a 500-ml. French-square bottle. Add 10 grams of filter aid and 350 ml. of methanol (ACS-grade). Roll the bottle and contents for 1 hour.

Filter the solids on a 71-mm. Büchner funnel. Press the solids with a teaspoon or other suitable instrument to squeeze out the methanol. Wash the bottle and solids with three 25-ml. portions of methanol, adding the wash solutions to the filtrate. Discard the solids and dilute the filtrate to 500 ml. with methanol.

Pipet a 200-ml. aliquot of the solution into a 1-liter separatory funnel. Add 500 ml. of water and 10 ml. of saturated sodium bicarbonate solution. Extract the xyleneol from the solution with one 100-ml. and two 50-ml. portions of benzene and combine the extract solutions in a 250-ml. separatory funnel. Extract the xyleneol from the benzene solution with two 25-ml. portions of 2*N* sulfuric acid and combine the extract solutions in a 250-ml. separatory funnel. Wash the acid extract solution with three 25-ml. portions of ether (A.R.-grade). Discard the washings. Continue the determination as described in the colorimetric procedure for 4-dimethylamino-3,5-xyleneol.

Subtract the absorbance owing to any apparent "xyleneol" found in a sample of control peaches to obtain the net absorbance. Determine the micrograms of 4-dimethylamino-3,5-xyleneol represented by the net absorbance by referring to a standard calibration curve and correct for per cent recovery of the "xyleneol" obtained from the peaches. Calculate parts per million as based on the weight of the sample represented by the aliquot of the methanol extract solution:

$$\frac{\mu\text{g. in aliquot}}{40} = \text{p.p.m. 4-dimethylamino-3,5-xyleneol}$$

**Recovery of 4-Dimethylamino-3,5-xyleneol Added to Peaches.** STANDARD SOLUTION 4. Dissolve 0.100 gram of 4-dimethylamino-3,5-xyleneol in methanol and dilute the solution to 1 liter with methanol. Concentration: 100  $\mu$ g. of the "xyleneol" per ml.

STANDARD SOLUTION 5. Dilute 25.0 ml. of standard solution 4 to 250 ml. with methanol. Concentration: 10  $\mu$ g. of the "xyleneol" per ml.

Grind a sufficient quantity of non-treated whole peaches with a meat grinder. Weigh 100 grams of ground peach in a 500-ml. French-square bottle. Using standard solution 5, add 0, 10, 20, 50, 100, 150, 200 or 250  $\mu$ g. of the "xyleneol" to cover the range desired. Then add 10 grams of filter aid and enough methanol to total 350 ml. of methanol. Roll the bottle and con-

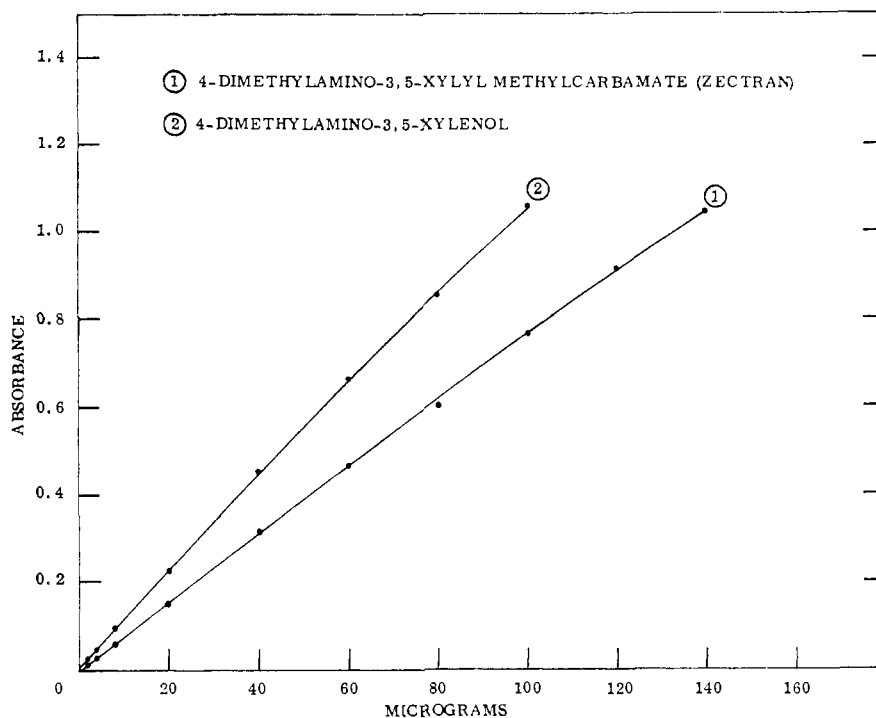


Figure 1. Standard calibration curves for 4-dimethylamino-3,5-xylyl methylcarbamate and 4-dimethylamino-3,5-xyleneol

tents for 1 hour. Continue the determination as in the procedure for 4-dimethylamino-3,5-xyleneol in peaches.

Determine the micrograms of 4-dimethylamino-3,5-xyleneol represented by the net absorbance by referring to the standard calibration curve. Calculate the per cent recovery as based on the amount of "xyleneol" represented by the aliquot of the methanol extract solution. Recovery data obtained by the authors are shown in Table I. Analysis of the nontreated ground peach itself showed an apparent "xyleneol" content of less than 0.03 p.p.m.

**Procedure for Determining 4-Dimethylamino-3,5-xylyl Methylcarbamate in Peaches.** Grind a sufficient quantity of treated whole peaches with a meat grinder. Weigh 100 grams of ground peach in a 500-ml. French-square bottle. Add 10 grams of filter aid and 350 ml. of methanol. Roll the bottle and contents for 1 hour.

Filter the solids on a 71-mm. Büchner funnel. Press the solids with a teaspoon or other suitable instrument to squeeze out the methanol. Wash the bottle and solids with three 25-ml. portions of methanol, adding the wash solutions to the filtrate. Discard the solids and dilute the filtrate to 500 ml. with methanol.

Pipet two 200-ml. aliquots of the methanol extract solution into respective 1-liter separatory funnels. Add 500 ml. of water and 10 ml. of saturated sodium bicarbonate to each solution. Extract the "carbamate" from each solution with one 100-ml. and two 50-ml. portions of benzene. Combine the ex-

tract solutions in respective 250-ml. separatory funnels. Extract the "carbamate" from each benzene solution with two 25-ml. portions of 2*N* sulfuric acid and combine the extract solutions in respective 250-ml. separatory funnels. Wash each acid extract solution with three 25-ml. portions of ether. Discard the washings. Continue the determination as in the colorimetric procedure for 4-dimethylamino-3,5-xylyl methylcarbamate.

Subtract the net absorbance owing to any apparent "carbamate" found in a sample of control peaches to obtain the net absorbance owing to the "carbamate." Determine the micrograms of 4-dimethylamino-3,5-xylyl methylcarbamate represented by the net absorbance by referring to the standard calibration curve and correct for per cent recovery of the "carbamate" obtained from the peaches. Calculate parts per million as based on the weight of the sample represented by the aliquot of the methanol extract solution.

**Recovery of 4-Dimethylamino-3,5-xylyl Methylcarbamate Added to Peaches.** STANDARD SOLUTION 6. Dissolve 0.100 gram of 4-dimethylamino-3,5-xylyl methylcarbamate in methanol and dilute the solution to 1 liter with methanol at refrigerator temperature. Store the solution in a refrigerator for long-time stability. Concentration: 100  $\mu$ g. of the "carbamate" per ml.

STANDARD SOLUTION 7. Dilute 25.0 ml. of standard solution 6 with methanol and keep the solution in a refrigerator. Concentration: 10  $\mu$ g. of the "carbamate" per ml.

Table II. Recovery of 4-Dimethylamino-3,5-xylyl Methylcarbamate in Peaches

Added, P.P.M.	Found, P.P.M.	Recovery, %
0.10	0.087	87
	0.097	97
0.20	0.168	84
	0.175	88
0.50	0.463	93
	0.439	88
1.00	0.872	87
	0.888	89
1.50	1.259	84
	1.342	89
2.00	1.712	86
	1.719	86
2.50	2.278	91
	2.307	92
3.00	2.924	97
	2.774	92
3.50	3.065	88
	3.199	91

Grind a sufficient quantity of nontreated whole peaches with a meat grinder. Weigh 100 grams of ground peach in a 500-ml. French-square bottle. Using standard solution 7, add 0, 10, 20, 50, 100, 150, 200, 250, 300, or 350  $\mu$ g. of the "carbamate" to cover the range desired. Then add 10 grams of filter aid and enough methanol to total 350 ml. of methanol. Roll the bottle and contents for 1 hour. Continue the determination as directed in the procedure for 4-dimethylamino-3,5-xylyl methylcarbamate in peaches.

Determine the micrograms of 4-dimethylamino-3,5-xylyl methylcarbamate represented by the net absorbance by referring to the standard calibration curve. Calculate the per cent recovery as based on the amount of "carbamate" represented by the aliquot of the methanol extract solution. Recovery data obtained by the authors are shown in Table II. Analysis of nontreated ground peach itself showed no apparent carbamate content. Recovery data obtained when known amounts of both 4-dimethylamino-3,5-xyleneol and 4-dimethylamino-3,5-xylyl methylcarbamate were added to 100-gram samples of nontreated ground peach are shown in Table III.

#### Determination of 4-Dimethylamino-3,5-xyleneol and 4-Dimethylamino-3,5-xylyl Methylcarbamate in Undelinted Cottonseed

**Reagents.** Same as already listed.

Benzene, 85%. Mix 850 ml. of benzene (thiophene-free) and 150 ml. of technical-grade toluene.

**Apparatus.** Same as already listed except the following which supplant the meat grinder and the 500-ml. French-square bottle:

Wiley mill. Screen with 6-mm. holes.

French-square bottle. Wide-mouthed, 1-liter, cap lined with polyethylene film.

**Table III. Recovery of Mixtures of 4-Dimethylamino-3,5-xyleneol and 4-Dimethylamino-3,5-xylyl Methylcarbamate in Peaches**

Xyleneol Added, P.P.M.	Carbamate Added, P.P.M.	Xyleneol Found, P.P.M.	Xyleneol Recovery, %	Carbamate Found, P.P.M.	Carbamate Recovery, %
0.10	0.10	0.076	76	0.093	93
		0.076	76	0.087	87
0.10	1.00	0.092	92	0.818	82
		0.103	103	0.853	85
1.00	0.10	0.815	82	0.080	80
		0.815	82	0.073	73
0.10	2.00	0.114	114	1.848	92
		0.116	116	1.844	92
2.00	0.10	1.820	91	0.067	67
		1.844	92	0.100	100

**Procedure for Determining 4-Dimethylamino-3,5-xyleneol in Undelinted Cottonseed.** Grind a sufficient quantity of treated undelinted cottonseed with a Wiley mill. Weigh 100 grams of ground cottonseed in a 1-liter French-square bottle. Add 20 grams of filter aid and 550 ml. of benzene. Roll the bottle and contents for 30 minutes.

Filter the solids on a 91-mm. Büchner funnel. Return the cottonseed to the bottle, leaving most of the filter aid on the funnel, and add 500 ml. of benzene. Roll the bottle and contents for 30 minutes. Filter the solids on the same Büchner funnel and combine the filtrates. Dilute the filtrate to 1 liter with benzene and discard the solids.

Pipet a 400-ml. aliquot of the extract solution into a 500-ml. separatory funnel. Extract the xyleneol from the solution with two 25-ml. portions of 2*N* sulfuric acid and combine the extract solutions in a 250-ml. separatory funnel. Wash the acid extract solution with three 25-ml. portions of ether. Discard the washings. Continue the determination as described in the colorimetric procedure for 4-dimethylamino-3,5-xyleneol. Calculate parts per million in the same manner as described in the procedure for the "xyleneol" in peaches.

**Recovery of 4-Dimethylamino-3,5-xyleneol Added to Undelinted Cottonseed.** Prepare standard solutions of 4-dimethylamino-3,5-xyleneol in the same manner as described in the procedure for recovery of 4-dimethylamino-3,5-xyleneol added to peaches but use benzene instead of methanol as the solvent.

Grind a sufficient quantity of nontreated undelinted cottonseed with a Wiley mill. Weigh 100 grams of ground cottonseed in a 1-liter, French-square bottle. Using the standard solution containing 10 µg. of the "xyleneol" per ml., add 0, 10, 20, 50, 100, 150, 200, or 250 µg. of the "xyleneol" to cover the range desired. Then add 20 grams of filter aid and enough benzene to total 550 ml. of benzene. Roll the bottle and contents for 30 minutes. Continue the determination as in the procedure for 4-di-

methylamino-3,5-xyleneol in undelinted cottonseed. Calculate the per cent recovery in the same manner as described for the recovery of "xyleneol" in peaches.

Recovery data obtained by the authors are shown in Table IV. Analysis of the nontreated cottonseed itself showed an apparent xyleneol content of less than 0.03 p.p.m.

**Procedure for Determining 4-Dimethylamino-3,5-xylyl Methylcarbamate in Undelinted Cottonseed.** Grind a sufficient quantity of treated undelinted cottonseed with a Wiley mill. Weigh 100 grams of ground cottonseed in a 1-liter French-square bottle. Add 20 grams of filter aid and 550 ml. of benzene. Roll the bottle and contents for 30 minutes.

Filter the solids on a 91-mm. Büchner funnel. Return the cottonseed to the bottle, leaving most of the filter aid on the funnel, and add 500 ml. of benzene. Roll the bottle and contents for 30 minutes. Filter the solids on the same Büchner funnel and combine the filtrates. Dilute the filtrate to 1 liter with benzene and discard the solids.

From two 400-ml. aliquots of the benzene solution in 500-ml. separatory funnels, respectively, extract the 4-dimethylamino-3,5-xylyl methylcarbamate with two 25-ml. portions of 2*N* sulfuric acid. Combine the extract solutions in respective 250-ml. separatory funnels. Wash each acid extract solution with three 25-ml. portions of ether. Discard the washings. Continue the determinations as in the colorimetric procedure for 4-dimethylamino-3,5-xylyl methylcarbamate. Calculate parts per million in the same manner as described in the procedure for the "carbamate" in peaches.

**Recovery of 4-Dimethylamino-3,5-xylyl Methylcarbamate Added to Undelinted Cottonseed.** Prepare standard solutions of 4-dimethylamino-3,5-xylyl methylcarbamate as described in the procedure for recovery of 4-dimethylamino-3,5-xylyl methylcarbamate added to peaches but use 85% benzene instead of methanol as the solvent.

Grind a sufficient quantity of non-

treated cottonseed with a Wiley mill. Weigh 100 grams of ground cottonseed in a 1-liter French-square bottle. Using the standard solution containing 10 µg. of the "carbamate" per ml., add 0, 10, 20, 50, 100, 150, 200, 250, 300 or 350 µg. of the carbamate to cover the range desired. Then add 20 grams of filter aid and enough benzene to total 550 ml. of extraction solvent. Continue the determination as in the procedure for 4-dimethylamino-3,5-xylyl methylcarbamate in undelinted cottonseed.

Calculate the per cent recovery obtained in the same manner as described for the recovery of "carbamate" in peaches. Recovery data obtained by the authors are shown in Table V. Analysis of the nontreated undelinted cottonseed itself showed no apparent "carbamate" content. Recovery data obtained when known amounts of both 4-dimethylamino-3,5-xyleneol and 4-dimethylamino-3,5-xylyl methylcarbamate were added to 100-gram samples of nontreated ground undelinted cottonseed are shown in Table VI.

**Table IV. Recovery of 4-Dimethylamino-3,5-xyleneol in Undelinted Cottonseed**

Added, P.P.M.	Found, P.P.M.	Recovery, %
0.10	0.103	103
	0.105	105
0.20	0.171	86
	0.176	88
0.50	0.449	90
	0.442	88
1.00	0.887	89
	0.887	89
1.50	1.347	90
	1.336	89
2.00	1.853	93
	1.830	92
2.50	2.211	88
	2.211	88

**Table V. Recovery of 4-Dimethyl-3,5-xylyl Methylcarbamate in Undelinted Cottonseed**

Added, P.P.M.	Found, P.P.M.	Recovery %
0.10	0.093	93
	0.090	90
0.20	0.193	96
	0.193	96
0.50	0.435	87
	0.456	91
1.00	0.894	89
	0.898	90
1.50	1.352	90
	1.391	93
2.00	1.874	94
	1.894	95
2.50	2.252	90
	2.174	87
3.00	2.702	90
	2.807	94
3.50	3.282	94
	3.326	95

## Discussion

These methods without modification determine 0.1 to 2.5 p.p.m. of 4-dimethylamino-3,5-xyleneol, 0.1 to 3.5 p.p.m. of 4-dimethylamino-3,5-xylyl methylcarbamate, or a total of 0.1 to about 3 p.p.m. of mixtures of the "xyleneol" and the "carbamate" in peaches and in undelinted cottonseed.

The methods for the residue determinations of 4-dimethylamino-3,5-xyleneol and 4-dimethylamino-3,5-xylyl methylcarbamate in peaches, using water as the water-miscible extraction solvent, should be generally applicable to the analysis of agricultural products with a high water content. The methods for the residue determinations in undelinted cottonseed, using benzene as the water-immiscible solvent, can be used on agricultural products containing oils and/or little water. Some modifications, of course, may be necessary.

**Table VI. Recovery of Mixtures of 4-Dimethylamino-3,5-xyleneol and 4-Dimethylamino-3,5-xylyl Methylcarbamate in Undelinted Cottonseed**

Xyleneol Added, P.P.M.	Carbamate Added, P.P.M.	Xyleneol Found, P.P.M.	Xyleneol Recovery, %	Carbamate Found, P.P.M.	Carbamate Recovery, %
0.10	0.10	0.095	95	0.093	93
		0.105	105	0.100	100
		0.111	111	0.872	87
0.10	1.00	0.105	105	0.859	86
		0.876	88	0.110	110
		0.831	83	0.090	90
1.00	0.10	0.111	111	1.914	96
		0.105	105	1.937	97
		1.759	88	0.133	133
2.00	0.10	1.759	88	0.133	133
		1.759	88	0.133	133

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## INSECTICIDE RESIDUES IN PROCESSED FOODS

### The Effect of Processing on Guthion Residues in Oranges and Orange Products

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Lake Alfred, Fla.

The use of Guthion on citrus necessitated a study of the distribution of residues in citrus by-products. A study was conducted on Guthion-treated oranges. It was found that standard washing procedure will remove 30% of Guthion residues from treated oranges. The remaining residue is entirely in the peel. Approximately 75% of the residue is destroyed during the treatment involved in production of citrus cattle feed.

GUTHION (trademark, Farbenfabriken Bayer), *O,O*-dimethyl *S*-4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl phosphorodithioate, is a widely used insecticide. Recently it has been registered for control of a large number of citrus pests including aphids, mites, scales, and brown snails. Extensive residue studies on this product have been conducted both in the authors' laboratories and in the Department of Entomology at the University of California, Riverside, Calif. The latter studies are reported elsewhere (1).

As cattle feed prepared from citrus waste is an important agricultural commodity, especially along the east coast of the United States, it was decided that a pilot plant study of the effect of processing on Guthion residues in various citrus by-products should be conducted. This study is reported in this paper. The citrus was processed in the pilot plant equipment at the Citrus Experiment Station, Lake Alfred,

Fla. The chemical analyses were all performed in the laboratories of Chemagro Corp., Kansas City, Mo.

## Materials and Methods

**Spray Treatments.** Pineapple oranges were sprayed with Guthion 25% wettable powder at the rate of 8 ounces active per 100 gallons of spray on December 12, 1961, and January 8, 1962. Control and treated fruit were picked January 22, 1962, and processed January 24. Sixty boxes (90 pounds each) of fruit were collected from both the treated and control plots.

**Processing Procedure.** Processing was carried out according to a standard commercial practice. A flow sheet of the over-all process is given in Figure 1. The washing procedure consisted of a light chlorine rinse, a brushing in a Pacrite Fruit Cleaner G. D. 3A Sudser, a second light chlorine rinse, and a germicidal wash using an 80-pound

pressure spray containing Ultrawet 60 L, trisodium phosphate, and a heavy chlorine concentration. The oranges were then put through water-eliminator rolls during which time they were given another light chlorine rinse. A final light chlorine rinse was made when the samples were on the conveyor. Rotten and split fruit were discarded.

Sixty boxes of fruit (approximately 5400 pounds) were used per run, but certain phases of each run were analyzed on a 20-box basis.

Juicing was carried out using a Food Machinery Corporation "In-Line Press" with the following settings: three short strainer tubes and two long strainer tubes, 0.040 and 0.090 inch, respectively; restrictor tubes,  $\frac{7}{16}$  inch; cutters,  $\frac{5}{8}$  inch long; beam setting, flush; r.p.m., 50. The finisher used was a Food Machinery Corporation Model 35 with screen openings of 0.020 inch and a head clearance of 0.002-0.006 inch.

The crude peel oil emulsion was