Removal of Azodrin Residues from Tomatoes by Commercial Preparative Methods

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Azodrin (3-[dimethoxyphosphinyloxy]-*N*-methyl-*cis*-crotonamide) was applied to tomatoes at rates of 1 and 2 lb per acre. The interval between treatment and harvest was 7 days after the second of two sprays and 4 hr after the third of three sprays. Harvest residues varied from 1.13 to 4.21 ppm of Azodrin. A cold wash removed 36 to 72% of the Azodrin residue, while a hot lye peel removed up to 93.4% of the residue. Tomato juice contained 0.22 to 0.59 ppm of Azodrin and canned tomatoes 0.14 to 0.35 ppm of Azodrin.

The insecticide Azodrin (3-[dimethoxyphosphinyloxy]-*N*-methyl-*cis*-crotonamide) has been suggested for control of fruit flies and aphids on tomatoes. Young and Bowman (1967) reported the occurrence and persistence of Azodrin residues on sweet corn. Fahey *et al.* (1969) showed that green beans treated with Azodrin contained 4.14 to 7.25 ppm of Azodrin and commercial canning processes removed 98% of the Azodrin residue. This study was conducted to determine the magnitude of Azodrin residues which might occur on tomatoes and to evaluate the effects of commercial processing on these residues.

SPRAY TREATMENT

Three plots four rows wide and approximately 200 ft long were prepared for residue studies, one of which was left as an untreated check. Each plot was divided into four replicates. On August 27 and September 2 two of the plots were treated with Azodrin (3.2 lb per gal emulsifiable) at rates of 1 and 2 lb active compound per acre in 100 gal of spray. Samples for residue studies were collected from each plot the morning of September 9 after which a third spray (at the same rate as previously employed) was applied.

SAMPLING AND PROCESSING

Samples of 80 lb of tomatoes (20 lb from each replicate) were picked the morning of Sept. 9 from the untreated plot and the plots treated with 1 and 2 lb of Azodrin on August 27 and Sept. 2. Then, 4 hr after a third application (on Sept. 9) samples were taken from the plots receiving three sprays. Ten unwashed tomatoes were taken from each replicate of each spray treatment and from the untreated plot for residue analysis.

The remaining tomatoes of each replicate were washed (unheated water) and a sample (10 tomatoes) taken for analysis. Samples of the washed tomatoes from each replicate were pressed for juice. Cans were filled with juice, salt added, heated to 85° C (190° F), then sealed and heated at 100° C (212° F) for 30 min.

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Tomatoes for canning, after the cold wash, were lye peeled [passed through an 18% sodium hydroxide solution heated to 82.5° C (180° F) in 30 sec and then washed with water to remove the skin and lye residue]. Samples of peeled tomatoes were taken for analysis. The tomatoes were placed in No. 303 cans, a 30-grain salt tablet added, and the can hot filled with cover juice, sealed, and processed at 100° C (212° F) for 45 min.

ANALYSIS

Whole tomatoes (unwashed, washed, peeled) were quartered, opposite quarters were blended in a Waring Blendor for 5 min, and 50-g samples transferred to 500-ml Erlenmeyer flasks. Canned tomatoes and canned juice were blended and a 50-g sample transferred to a 500-ml flask. One hundred grams of anhydrous sodium sulfate and 200 ml of methylene chloride were added to the sample and it was shaken for 30 min. The methylene chloride residue solution was filtered and stored until analyzed.

Twenty-five milliliters of ethyl acetate and 1 g of acid washed Norit-A (neutral) were added to 50 ml of the residue solution and shaken for 5 min. The charcoal was removed on a sintered glass filter and washed with three 10-ml volumes of ethyl acetate. The solvent was removed in a rotary evaporator and the residue solution diluted to appropriate volume, with ethyl acetate, for analysis by glc.

The glc analysis was made on a Varian Aerograph Model 1200 instrument equipped with a cesium bromide phosphorus detector set at EC-1 range and attenuation of 2 to 8. Gas chromatographic column, 5 ft × $^1/_4$ in. o.d. glass, packed with a 1 to 1 mixture of 5% OF-1 and 2% Reoplex 400 on 60- to 80- mesh Gas Chrom Q. Critical temperatures were column oven 195° C, injector 235° C, and detector 205° C. Gas flow rates were He (carrier gas) 75 ml per min, H at 50 ml per min, and air at 190 ml per min.

Retention time for Azodrin was 1.36 min. Only Azodrin was found in residue samples at levels exceeding 0.1 ppm.

RESULTS

Table I shows the recovery of Azodrin from fortified samples. Recovery ranged from 90 to 100% of the Azodrin added. The average recoveries were: 94.5% with unwashed

Table I. Recovery of Azodrin from Tomato Products

Tomato Sample	Azodrin Added		Azodrin Found	
	μg	ppm	μg	%
Unwashed	0	0	0	
Unwashed	5	0.1	4.72	94.5
Unwashed	100	2.0	94.5	94.5
Washed	0	0	0	
Washed	5	0.1	4.92	98.5
Washed	50	1.0	50.0	100.0
Peeled	0	0	0	
Peeled	5	0.1	4.96	99.2
Peeled	25	0.5	24.6	98.4
Canned	0	0	0	
Canned	5	0.1	4.84	96.8
Canned	25	0.5	23.5	94.0
Juice	0	0	0	
Juice	5	0.1	4.5	90.0
Juice	25	0.5	24.2	96.8

tomatoes; 99.3% with washed tomatoes; 99.3% with peeled tomatoes; 95.4% with canned tomatoes; and 93.4% with tomato juice.

Table II shows the effect of processing on Azodrin residues. The residues found on harvested tomatoes approximated 1 to 2 ppm (at 1 and 2 lb per acre) when the final spray was applied 7 days before picking. The residue increased to 3.16 and 4.21 ppm when samples were picked within 4 hr of the final (third) spray.

The cold wash removed from 36 to 72% of the residue found on unwashed tomatoes. The hot lye peel removed 72.5 to 93.4% of the residue.

The residues found in tomato juice after canning were 0.22 to 0.28 ppm of Azodrin from the 1 lb per acre treatment and 0.52 to 0.59 ppm of Azodrin from the 2 lb per acre treatment. Canned whole tomatoes contained 0.14 ppm of Azodrin from the 1 lb per acre treatment and 0.32 to 0.35 ppm from the 2 lb per acre treatment.

Table II. Azodrin Residues on Processed Tomatoes, 1969

Process	PPM of Azodrin[a]				
	Untreated	Two Sprays[b]		Three Sprays[c]	
		1 lb	2 lb	1 lb	2 lb
Unwashed	<0.10	1.13	2.03	3.16	4.21
Cold Washed	<0.10	0.33	1.30	0.88	1.40
Hot Lye Peeled	<0.10	0.14	0.56	0.21	0.49
Canned					
Juice	<0.10	0.28	0.52	0.22	0.59
Whole Tomato	<0.10	0.14	0.35	0.14	0.32

[a] Average of four replicates. [b] Final spray Sept. 2, 7 days before picking. [c] Final spray Sept. 9, 4 hr before picking.

DISCUSSION

The canned tomato juice after processing contained from 25% to 85% of the Azodrin residue present on cold washed tomatoes from which it was prepared. The canned whole tomatoes contained from 62.5% to 100% of the residue found on hot lye peeled tomatoes used in canning. These observations suggest that appreciable residue remained in the pulp from which the juice was pressed, and that the final heating process had only a limited effect on the residue present.

LITERATURE CITED

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Received for review June 12, 1970. Accepted September 14, 1970. Journal Paper No. 4038, Purdue University Agricultural Experiment Station. Work supported in part by Shell Chemical Co.