Removal of DDT, Parathion, and Carbaryl from Spinach by Commercial and Home Preparative Methods

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Spinach grown on three separate plots was treated with DDT, parathion, and carbaryl. After harvesting, it was prepared for consumption by commercial canning and home cooking, freezing, and canning, and residue determinations were made at appropriate points. Minimum and maximum commercial washing removed 17 and 48% of the DDT, 0 and 9% of the parathion, and 66 and 87% of the carbaryl, respectively. Use of a detergent in the wash water increased the per cent removal. After commercial water blanching, 38 to 60% of the DDT was removed, 49 to 71% of the parathion, and 96 to 97% of the carbaryl. Steam blanching removed little or no residue. After commercial canning and storage for 5 months, no DDT remained, but small amounts of TDE and DDE were found; parathion and carbaryl did not change. The p,p' isomer of DDT decreased more than the o,p' isomer during washing and blanching. Home and commercial washing removed comparable amounts of DDT and carbaryl. Little or no change in residue occurred after cooking washed spinach without the addition of water. Storage of raw spinach at 45° F. for 15 and 13 days caused no significant change in DDT and parathion.

L imited data are available on the effect of washing and processing spinach in reducing pesticide residue levels. Brittin and Fairing (1950) evaluated the processing loss of DDT and parathion by colorimetric methods. Farrow et al. (1966) found that p,p'-DDT was partially converted to p,p'-TDE[2,2-bis(p-chlorophenyl)-1,1-dichloroethane] during the processing of canned spinach. Ralls et al. (1966) studied the residue levels of diazinon and its transformation products at various steps in the preparation of spinach for preservation. The removal of DDT, malathion, and carbaryl residues during commercial and home preparation of tomatoes (Farrow et al., 1968) and of DDT residues from potatoes (Lamb et al., 1968) has been studied by this laboratory. The work reported is a continuation of the studies on removal of pesticide residues from vegetable products by commercial and home preparative procedures.

EXPERIMENTAL

Pesticide Application. Spinach, CPC No. 44 variety, was grown on a commercial field near Soledad, Calif. The field was treated with 230 grams (0.5 pound) per acre of phosdrin and 110 grams (0.25 pound) per acre of parathion approximately 6 weeks before the start of the experimental program.

Each pesticide was applied to a separate plot, each 0.01 acre (13.2 by 33 feet). Two plots were in a portion of a field scheduled for harvest approximately April 5; the third was in a separate portion of the same field scheduled for

harvest 2 weeks later. Each plot was sprayed once with 1 gallon of diluted spray using a Hudson sprayer, equipped with flat spray nozzles on triple boom heads.

The following treatments were applied:

Plot 1. Parathion, Soil Serve emulsifiable concentrate, 4 pounds per gallon. March 29, 230 grams (0.5 pound) per acre. Harvested April 5 (7 days after spraying)

Plot 2. Carbaryl, Stauffer Flowable Sevin, 4 pounds per gallon. April 5, 0.9 kg. (2.0 pounds) per acre. Harvested April 12 (7 days after spraying)

Plot 3. DDT, 50% wettable powder (Ortho). April 5, 2.7 kg. (6.0 pounds) per acre. Harvested April 18 (13 days after spraying)

The spinach was cut 2 to 3 inches above the ground and packed in fiberboard cartons without liners. Approximately 45 kg. (100 pounds) of spinach from each plot were shipped to Washington, D. C., by air express on the afternoon of the day it was harvested, arriving at its destination the following morning. A duplicate set of harvested samples from the plots was transported to the Berkeley Laboratory and processed the following day, except that the DDT-treated samples were placed in cold storage and processed April 20, two days after harvest.

In an effort to obtain residues at or near tolerance levels, pesticides were applied in such a way as to leave higher residues at time of harvest than would result from usual commercial applications. It was not always possible to predict in advance what these residues would be, and with DDT, the resulting residues exceeded the tolerance established by the U. S. Food and Drug Administration severalfold, because of application of DDT at a more advanced stage of growth and closer to harvest than the maximum application specified by the U. S. Department of Agriculture (1967). Parathion and carbaryl also exceeded tolerance limits as a result of application closer to harvest than the minimum specified time.

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Commercial Preparation. Spinach was subjected to commercial canning and freezing procedures at the Berkeley Laboratory. Special equipment at this laboratory included an experimental washer and blancher designed to duplicate commercial procedures on a pilot plant scale. The equipment consisted of a spray immersion unit used for both washing and blanching the spinach, and a rotary spray unit for additional washing. The residence time in each unit and the temperature and pressure of sprays could be controlled. Water was recirculated in each unit.

The spinach was trimmed to separate the clusters of leaves and remove coarse stem material, and the entire lot was mixed thoroughly. Six 450-gram samples were placed in polyethylene bags and held in the freezer until they could be analyzed. The remaining spinach was divided into three portions of about 13.5 kg. (30 pounds) each. Commercial processing procedures are outlined in Figure 1.

MINIMUM WASH. The spinach was run through the spray immersion section of the experimental washer with water at about 21° C. (70° F.). The residence time in the washer was 65 seconds, the spray pressure was 30 pounds, and the water volume was 20 gallons. The water was recirculated. After washing, three more 450-gram samples were frozen in polyethylene bags. The remaining spinach was divided into two equal portions for water and steam blanching.

MAXIMUM WASH. The spinach was washed in the spray immersion washer as described above with fresh water and then run through the rotary spray washer. The temperature of this unit was about 21° C. (70° F.), the spray pressure 20 pounds, and the speed of rotation 10 r.p.m. The residence time was 30 seconds. The reel was 40 inches long and 18 inches in diameter. Following this wash, three more 450-gram samples were frozen in polyethylene bags and the remaining spinach was divided into two equal portions.

MAXIMUM WASH, DETERGENT. The spinach was washed exactly as described above, but 0.1% Tergitol 08 was added to the spray immersion unit. The detergent solution was removed by passage through the rotary spray washer using pure water. Three 450-gram samples were frozen in polyethylene bags and the remaining spinach was divided into two equal portions.

WATER BLANCH, CANNED. The water blanching was performed in the spray immersion unit filled with fresh water after heating the water to 85° C. (185° F.). Since the maximum residence time in this unit is 65 seconds, the conveyor belt running through the unit was run intermittently for 10 seconds out of each minute giving a total blanching time of 6.5 minutes. The spinach was sampled continuously as it emerged from the blancher. Three 450-gram samples were collected, placed in polyethylene bags,
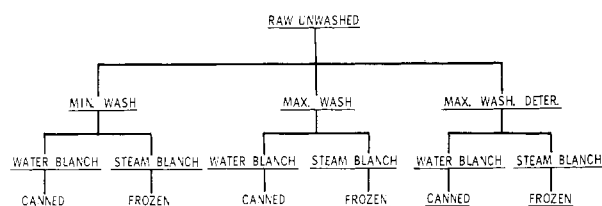
immersed in a large volume of cold water until cold, and then frozen.

The remaining spinach was drained and 340 grams (12 ounces) filled into each of 12 No. 303 cans. A salt tablet containing 3 grams of NaCl was put at the bottom of each can before filling. The cans were filled with hot water at 88° to 94° C. (190° to 200° F.), exhausted for 5 minutes at 99° to 100° C. (210° to 212° F.) in a steam chamber, then closed and processed for 50 minutes at 122° C. (252° F.) in a still retort. They were then water-cooled in the retort to approximately 38° C. (100° F.).

STEAM BLANCH, FROZEN. Spinach was spread out in a thin layer and placed in a steam chamber where it was subjected to live steam at 100° C. (212° F.) for 2 minutes. The spinach was drained on a wire-mesh screen and nine 1-pound samples were filled into polyethylene bags. The sealed bags were immersed in cold water until cold and then placed in a plate freezer where they were held until analyzed.

Home Preparation and Storage. Each of the three lots of spinach was received in Washington, D. C., on the day following harvest. The total weight of the DDT-treated spinach was 54 kg. (120 pounds), the carbaryl-treated spinach 57 kg. (125 pounds), and the parathion-treated spinach 68 kg. (145 pounds). The home preparative procedures are outlined in Figure 2. On the day the spinach was received, the extraction of all samples connected with the washing and blanching for home freezing was completed. The extraction of all samples connected with the home cooking experiments was completed after storage of the raw spinach for 4 or 5 days at approximately 7° C. (45° F.).

RAW WASHED. The spinach was washed by immersing in cold water and gently rubbing the leaves by hand.

BLANCHED FROZEN. The spinach was immersed in boiling water for 1.5 minutes in a sauce pan, the hot water drained off, and the spinach covered promptly with cold water. The spinach was then drained, triplicate samples were extracted for residue analyses, and the remainder was frozen.

FROZEN COOKED. The spinach was heated in a sauce pan without the addition of water.

COOKED. The raw washed spinach without added water was placed in a saucepan, cooked for 8 minutes, and allowed to cool. Triplicate samples were extracted for residue analysis.

STORED. Raw, unwashed spinach sprayed with DDT was stored in a refrigerator at approximately 7° C. (45° F.) for 15 days and the parathion-treated spinach for 13 days.

Figure 1. Sampling points for commercial spinach preparation
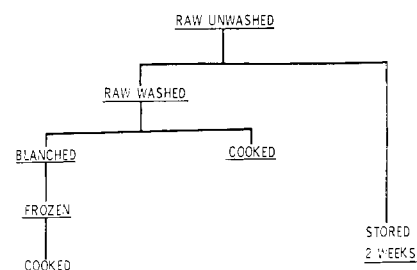

Figure 2. Sampling points for spinach home preparative procedures

A storage experiment was not performed on the carbaryl-treated spinach. Five or six subsamples were analyzed at regular intervals during these storage periods.

Analytical Methods. The procedure for the extraction of DDT from the spinach and the cleanup of the extract for analysis was essentially that of Mills (1959). Petroleum ether extracts were stored at reduced temperatures until analyzed. The extract was cleaned up in a Florisil column and eluted with 6% ethyl ether in petroleum ether. Extracts were analyzed by gas-liquid chromatography (GLC) using electron-capture detectors. The Washington, D. C., laboratory used a Packard 800 with a 6-foot by $^1/_4$-inch borosilicate glass column and the Berkeley laboratory used a Wilkens Hy Fi with a 10-foot by $^1/_8$-inch borosilicate glass column. Both used a packing mixture of equal amounts of 10% DC 200 silicone grease and 15% QF-1 on Gas Chrom Q (Burke and Holswade, 1966). Both were operated at 200° C. with nitrogen flow rates of 120 and 40 ml. per minute in the Packard and the Wilkens, respectively.

Parathion was determined in the Washington laboratory by GLC (Guiffrida, 1964) following a sweep codistillation cleanup procedure (Storherr and Watts, 1965). In the Berkeley laboratory, parathion was determined by the official AOAC method (Association of Official Agricultural Chemists, 1965) with the following modifications: The sample was extracted with isopropyl alcohol–benzene mixture. Five grams of the adsorbent mixture was used per 100 ml. of benzene extract. In the final filtration, the filter was washed and the filtrate made to volume with 50% ethanol solution instead of water. A blank reading was made on each sample just before addition of the final reagent. By use of the above method, recoveries of added amounts of parathion to untreated spinach ranged between 74 and 88%.

Carbaryl was determined in both laboratories by the method of Benson and Finocchiaro (1965), except that absorbance readings were taken 30 seconds after addition of the color reagent. In the Berkeley laboratory, carbaryl was determined on the canned spinach by thin-layer chromatography (Finocchiaro and Benson, 1965). Recoveries were somewhat variable, ranging from approximately 60% at 1 p.p.m. to 90% or better at 10 p.p.m.

RESULTS AND DISCUSSION

Sample Variation and Storage Effects. Data on the effect of storing spinach samples treated with DDT and parathion are shown in Tables I and II, respectively. An

Table II. Behavior of Parathion during Storage of Spinach at 7° C.

No. of Days Stored	Residue, P.P.M.
1	1.72 (0.56)
3	1.37 (0.30)
5	1.34 (0.53)
7	1.32 (0.46)
9	1.44 (0.24)
13	1.51 (0.68)

[a] 95% confidence limits (wet basis) = SD (Student's t at 0.5)/$\sqrt{N}$.

analysis of variance indicates that storage for periods up to 15 days at 7° C. (45° F.) for DDT and 13 days for parathion does not affect the residue level. No change is apparent in the ratio of p,p' and o,p' isomers of DDT as a result of storage.

The standard deviation for a single sample is about 20% of the mean for DDT and 25% for parathion. Confidence limits at the 95% level have been tabulated for all averages as an indication of their variability.

Removal of DDT by Commercial Preparative Procedures. Data obtained in the commercial preparative procedures are shown in Table III. An average of 27.3 p.p.m. of DDT was found on the unwashed spinach with confidence limits of 5.5 p.p.m. at the 95% level. Of the total DDT, approximately 90% consisted of the p,p' isomer and 10% of the o,p' isomer. Concentrations of p,p'-DDE [1,1-dichloro-2-bis(p-chlorophenyl) ethylene] amounting to 0.2 p.p.m. or less were found in the unwashed spinach; however, these amounts were small in relation to the total DDT that was present, and quantitative estimations were not made.

The efficiency of the washing procedure made a statistically significant difference in the amount of DDT removed, varying from 17% removal after the minimum wash to 73% after the maximum wash with detergent. Water blanching caused an apparent decrease of DDT when results are expressed on the dry basis, except in the case of the detergent-washed spinach.

The o,p' isomer of DDT showed an increase in concentration after blanching over that contained in the raw unwashed spinach, whereas the p,p' isomer showed a marked decrease. The ratio of o,p'-DDT to p,p'-DDT increased after all operations involving leaching of the product.

Table I. Behavior of DDT Residues during Storage of Spinach at 7° C.

Residues in p.p.m.

	Days after Harvest					
	1	3	8	10	12	15
p,p' Isomer	17.6 (2.8)[a]	19.2 (4.5)	19.3 (4.6)	19.5 (1.5)	15.8 (3.5)	17.9 (2.5)
o,p' Isomer	2.5 (0.5)	2.7 (0.8)	2.3 (0.9)	2.6 (0.3)	1.6 (0.5)	2.0 (0.4)
DDE	0.17 (0.03)	0.19 (0.02)	0.16 (0.06)	0.19 (0.02)	0.15 (0.03)	0.18 (0.02)
Total DDT[b]	20.2 (3.0)	22.1 (5.2)	21.8 (5.2)	22.3 (1.8)	17.5 (4.1)	20.1 (2.9)
% Solids	13.62	14.56	14.10	13.49	14.15	13.45

[a] 95% confidence limits (wet basis) = SD (Student's t at 0.05)/$\sqrt{N}$.
[b] Including DDE.

Residues in p.p.m.

Treatment[a]	% Solids	p,p'-DDT	o,p'-DDT	p,p'-DDE	Total DDT and Related Compounds	% Decrease Wet	% Decrease Dry
By Commercial Procedures							
Unwashed	10.7	24.4	2.9	<0.2	27.3 (5.5)[b]	...	...
Raw washed							
W1	7.2	12.5	2.7	<0.2	15.2 (3.4)	45	17
W2	6.5	6.3	1.7	<0.2	8.0 (1.6)	71	48
W2D	6.6	3.4	1.4	<0.2	4.6 (0.6)	83	73
Water-blanched							
W1	9.1	9.9	4.0	0.4	14.3 (8.6)	48	38
W2	7.9	5.6	2.3	0.2	8.1 (1.1)	71	60
W2D	9.7	7.6	3.3	0.3	11.2 (1.4)	59	55
Steam-blanched							
W1	11.4	22.9	6.4	0.5	29.8 (13.6)	9[c]	3[c]
W2	12.1	6.5	3.2	0.3	9.9 (3.1)	64	68
W2D	10.7	5.1	2.1	0.2	7.4 (1.0)	73	73
Canned, water-blanched[d]							
W1	5.7	n.d.	n.d.	0.1	2.1[e] (1.4)	92	86
W2	5.6	n.d.	n.d.	0.1	1.4[e] (0.1)	95	91
W2D	5.6	n.d.	n.d.	0.2	1.5[e] (0.5)	95	89
By Home Preparative Procedures							
Unwashed	13.6	17.6	2.5	0.17	20.2 (3.2)[b]	...	...
Washed	10.4	8.9	1.7	0.10	10.7 (1.3)	47	30
Blanched	8.8	5.0	1.2	0.07	6.3 (1.3)	69	52
Cooked	9.9	7.3	1.6	0.11	9.0 (3.2)	55	39

[a] W1 = minimum wash, W2 = maximum wash, W2D = maximum wash with detergent.
[b] 95% confidence limits (wet basis) = SD (Student's t at 0.05)/$\sqrt{N}$.
[c] Per cent increase.
[d] Stored 5 months.
[e] Includes p,p'-TDE.
    n.d. = not detected.

Explanations of observations of this type include isomeric transformations, differences in stability, and solubility differences. A possible explanation in this instance is that the o,p' isomer is more readily absorbed by the plant tissues than the p,p' isomer, probably as a result of its greater solubility in plant waxes. This would cause it to be more persistent under field conditions and more resistant to removal by washing and blanching. The apparent increase in the concentration of the o,p' isomer may be explained in part by the unavoidably large sampling variations characteristic of pesticide residue studies in green leafy crops and also by errors caused by the preferential leaching of soluble solids.

Neither water blanching nor steam blanching significantly decreased the residue of the washed spinach, taking into consideration the variability of the product (Table IV). A slight increase in residue was obtained in the minimum-washed samples after steam blanching; however, the magnitude of this increase is well within confidence limits and is probably not significant.

Variations in the amount of residue were of considerably greater magnitude in the samples given the minimum wash than in the more thoroughly washed samples, particularly after blanching and after processing. A possible explanation is that the poor wash may have exaggerated differences in different portions of the lot because of unequal exposure of the spinach to the wash water. The more thorough washes may have tended to minimize these differences by

more complete removal of residue from the more highly contaminated portions of the lot than from the less highly contaminated portions.

Unlike data obtained on other products and pesticides, water blanching was not more effective than steam blanching for the removal of DDT from spinach. The leaching of soluble solids during water blanching could account for this apparent inconsistency when results are expressed on the dry solids basis. A loss of soluble solids would give erroneously high values for the concentration of residues when calculated in this manner. Expressing results on the

Table IV. Loss of Dry Solids from Spinach after Water and Steam Blanching

	% Total Solids	Weight of Spinach, G.	Weight of Dry Solids, G.	% Loss of Solids
Before blanching	6.35	200	12.70	...
After water blanching	5.62	169	9.50	28.0
Before blanching	6.08	200	12.16	...
After water blanching	5.77	149	8.57	28.9
Before blanching	6.42	200	12.84	...
After steam blanching	6.48	176	11.39	11.2
Before blanching	5.25	200	10.50	...
After steam blanching	6.44	150	9.66	8.0

wet basis is equally in error, since spinach picks up a highly variable amount of water from the wash and blanch. Steam-blanched samples pick up less water than water-blanched samples and as a consequence are always higher in solids.

To obtain information on the magnitude of the leaching error, spinach purchased on the fresh market was trimmed and washed, and a weighed quantity was blanched in laboratory equipment using the same times and temperatures as in the pilot plant experiment. The spinach was weighed again after blanching and total solids were determined on representative portions before and after blanching (Table IV).

The loss of dry solids was calculated by subtracting the weight of dry solids in the blanched spinach from the weight of dry solids in the spinach before blanching. The loss of soluble solids during blanching is sufficient to produce a highly significant error in the residue levels calculated on the dry basis. This may be as much as 30% and 20% more solids which may be lost by water blanching than by steam blanching. Results obtained in the laboratory experiment are only an approximation of the leaching losses that occurred in the pilot plant experiment, since different spinach was used, and the actual blanching conditions in the pilot plant could not be duplicated in the laboratory. A similar experiment could not be run using the pilot plant equipment because all of the spinach entering the blancher cannot be recovered in a batch-type operation. It is apparent that the results reported in this study are subject to a significant error which would indicate less favorable removal of residues after blanching than was actually the case.

Analysis of the processed samples performed approximately 5 months after canning did not reveal the presence of any DDT in the spinach. Small amounts of p,p'-TDE and p,p'-DDE were found, and the total of these DDT-related compounds indicated an over-all loss of about 90% of the DDT present in the raw unwashed spinach. This represents a considerable decrease in the amount of DDT present in the water-blanched spinach and indicates conversion of a large proportion of the DDT originally present in the can to compounds not detected by the method of analysis that was used.

In the work reported by Farrow *et al.* (1966) only partial conversion of p,p'-DDT to p,p'-TDE was found and a considerable portion of the DDT remained unchanged; however, in the earlier work, the spinach was subjected to much less heating. Small thin cans known as thermal death time cans were used in the work of Farrow *et al.* and because of the rapid rate of heat penetration into these cans as compared with the commercial No. 303 cans used in the present work, much less heat was required to produce the same sterilizing values. In earlier unpublished work in this laboratory, p,p'-DDT was completely lost on processing spinach in commercial size cans. The conversion of p,p'-DDT to p,p'-TDE in various other systems has been reviewed (Ott and Gunther, 1965).

Removal of DDT Residues by Home Preparative Procedures. Data obtained in the home preparative experiments are shown in Table III.

The cold water wash removed 30% of the total DDT residue on the dry basis (47% on the wet basis), inter-

mediate between that removed in the minimum and maximum commercial washes. Blanching removed 52% of the residue (69% on the wet basis), again intermediate between the minimum and maximum commercial water and steam blanches.

Cooking the spinach using only the water adhering after the wash decreased the residue only 39% on the dry basis (55% on the wet basis). In view of the high degree of variability of these results, the amount of residue found is not significantly different from that found on the washed samples, indicating that cooking under these conditions can have no pronounced effect on the DDT present. The limited amount of heating given these samples did not convert p,p'-DDT to p,p'-TDE.

The ratio of the isomers of DDT changed slightly following operations likely to produce leaching, but not to as marked an extent as in the commercially prepared samples. Here again less of the o,p' isomer than of the p,p' isomer was lost during washing and blanching.

Parathion Removal. Data on the removal of parathion from spinach by commercial preparative procedures and by home preparative procedures are summarized in Table V.

The apparent decrease in parathion during the commercial washing of spinach is due primarily to the pickup of water. Expressed on the dry basis, the loss of parathion is statistically insignificant, except for the detergent wash which removed approximately 24% of the residue. Commercial water blanching removed significant amounts of residue in all instances. The low residues found in the blanched spinach given the maximum water wash without detergent appear abnormal, since differences between the maximum water wash with and without detergent were not significant in the steam-blanched and the canned samples. Probably water blanching removed slightly more than one half the residue and there were no differences among the three washing treatments after the spinach was water-blanched.

Steam blanching produced little or no reduction of parathion and increased the apparent concentration of residue because of the loss of moisture from the spinach. The steam blanching was carried out without a spray rinse, and the spinach was cooled by sealing it in a polyethylene bag and immersing the bag in running water. Reduction of residue might have been greater had the spinach been cooled under water sprays, a frequent commercial practice. The leaching of soluble solids, particularly during water blanching, may have caused an apparent increase in the concentration of parathion.

Processing caused little or no further reduction in parathion. There is an indication that the parathion in the canned samples given the maximum washing treatment is slightly less than that in the samples given the minimum wash, but the difference is of little or no practical significance. The over-all reduction of parathion as a result of commercial canning is about 60% on the dry solids basis or 80% on the wet basis.

In the home preparation series of experiments the washed spinach contained 39% less parathion on the dry basis than the unwashed; however, the blanched and frozen samples showed no significant reduction. It may be concluded, therefore, that any reduction of parathion during blanching

Table V. Removal of Parathion from Spinach

Treatment[a]	% Solids	Residues in p.p.m. Av. Parathion	% Decrease Wet	% Decrease Dry
		By Commercial Processing		
Unwashed	12.3	1.5 (0.2)[b]	...	...
Raw, washed				
W1	7.2	0.87 (0.17)	42	0
W2	7.2	0.80 (0.03)	47	9
W2D	6.9	0.65 (0.10)	57	24
Water-blanched				
W1	9.2	0.49 (0.04)	67	58
W2	9.1	0.32 (0.01)	79	71
W2D	8.2	0.51 (0.05)	66	49
Steam-blanched				
W1	10.8	1.3 (0.1)	13	0
W2	10.2	1.1 (0.2)	27	13
W2D	11.8	1.2 (0.1)	20	17
Canned				
W1	6.0	0.32 (0.06)	79	58
W2	5.5	0.23 (0.04)	85	66
W2D	5.6	0.25 (0.08)	83	64
		By Home Preparative Procedures		
Unwashed	13.8	1.7 (0.6)[b]	...	...
Washed	9.7	0.73 (0.24)	57	39
Blanched	8.8	1.1 (0.2)	35	...
Frozen	...	1.1 ...	35	...
Cooked (fresh)	10.7	1.2 (0.2)	29	11

[a] W1 = minimum wash, W2 = maximum wash, W2D = maximum wash with detergent.
[b] 95% confidence limits (wet basis) = SD (Student's t at 0.05)/$\sqrt{N}$.

and freezing is within the confidence limits of this experiment and probably of little significance.

Cooking produced no further reduction of parathion. The over-all effectiveness of removal was less in the home preparative procedures than in the commercial procedures when water blanching was used. Less moisture was picked up during the household cooking procedure than during commercial canning, since the spinach was cooked without added water other than that adhering to the leaves from the washing. This resulted in higher residues in the home-cooked spinach than in the canned spinach by about a factor of 4 when results are reported on the wet basis.

Carbaryl Removal. Data on the removal of carbaryl from spinach by commercial and home preparative procedures are summarized in Table VI.

Commercial washing removed from 66 to 88% of the residue present on the raw spinach. The thoroughness of the wash was a definite factor, the maximum wash reducing the residue level to about one third of that present after the minimum wash. The use of a detergent made only an insignificant difference in the amount removed.

Commercial water blanching reduced the level of carbaryl to less than 5% of that originally present. After water blanching there was no significant difference among the three washing treatments. As previously stated, the leaching of soluble solids produces a significant positive error in the results when expressed on the dry basis.

Except for the sample given the minimum wash, steam blanching did not remove a significant amount of residue. Although steam blanching removed approximately one third of the residue in the minimum washed spinach when expressed on the dry basis, it still remained significantly

higher in residue than the steam-blanched samples given the maximum washing treatment. The steam-blanched samples were not cooled in a water spray after blanching, so there was little opportunity for leaching to occur during this operation. The loss of moisture tends to increase the residue when expressed on the wet basis.

Apparent carbaryl significantly increased in the processed samples when determined by the colorimetric method (Benson and Finocchiaro, 1965). Since this increase appeared to be caused by the production of interfering substances during heating of the spinach, samples were tested by the thin-layer chromatographic method of Finocchiaro and Benson (1965); results were much lower and showed all of the processed samples to contain 0.05 p.p.m. or less carbaryl. Determinations by the colorimetric method on unheated spinach not treated with carbaryl gave blank readings equivalent to about 0.2 p.p.m. carbaryl; it is concluded that the interference is not serious in unheated samples at the levels found in those samples. Finocchiaro and Benson stated that the lower limit of the colorimetric method is about 0.2 p.p.m.

The data indicate that carbaryl is reduced to insignificant levels in the processed spinach. It is difficult to assess the actual amount of carbaryl destroyed in processing, since the amount present in the blanched spinach is approaching the limit of analytical uncertainty of the colorimetric method, and the thin-layer chromatography method employed on the processed spinach is not capable of high precision. Our results indicate that the commercial preparative procedures normally employed are capable of reducing carbaryl residues to levels within the sensitivity of analytical procedures commonly employed for this pesticide.

Table VI. Removal of Carbaryl from Spinach

Residues in p.p.m.

Treatment[a]	% Solids	Average Carbaryl	% Decrease Wet	Dry
		By Commercial Processing		
Unwashed	9.0	20.8 (4.3)[b]	. . .	. . .
Raw, washed				
W1	6.0	4.8 (1.4)	77	66
W2	6.5	2.0 (0.4)	90	87
W2D	5.9	1.6 (0.1)	92	88
Water-blanched				
W1	8.3	0.72 (0.22)	97	96
W2	6.9	0.49 (0.14)	98	97
W2D	7.6	0.48 (0.02)	98	97
Steam-blanched				
W1	11.1	5.2 (0.4)	75	80
W2	9.8	3.1 (0.7)	85	86
W2D	9.9	3.4 (0.4)	84	85
Canned				
W1, W2, and W2D	5.1	Tr[c] . . .	99+	99+
		By Home Preparative Procedures		
Unwashed	11.9	19.7 (6.4)[b]	. . .	. . .
Washed	9.0	4.5 (3.1)	77	70
Cooked (fresh)	7.1	4.6 (2.6)	77	61
Blanched	9.6	1.2 (0.5)	94	93
Frozen	. . .	1.8 (0.6)	91	. . .
Cooked (frozen)	. . .	1.6 (1.4)	92	. . .

[a] W1 = minimum wash, W2 = maximum wash, W2D = maximum wash with detergent.
[b] 95% confidence limits = SD (Student's t at 0.05)/$\sqrt{N}$.
[c] Tr = less than 0.05 p.p.m.

Washing spinach using home procedures removed 70% of the carbaryl present on the unwashed spinach, intermediate between the minimum and maximum commercial washes. Home cooking did not remove any additional residue. Blanching for home freezing removed a small additional amount of residue of doubtful significance. Removal of carbaryl by home preparative procedures commonly employed for this vegetable may be considered satisfactory.

LITERATURE CITED

Association of Official Agricultural Chemists, "Official Methods of Analysis," 10th ed., p. 403, Section 24, 168, 1965.
Benson, W. R., Finocchiaro, J. M., J. Assoc. Offic. Agr. Chemists 48, 676 (1965).
Brittin, W. A., Fairing, J. D., J. Assoc. Offic. Agr. Chemists 33, 599 (1950).
Burke, J. A., Holswade, W., J. Assoc. Offic. Anal. Chemists 49, 374 (1966).
Farrow, R. P., Elkins, E. R., Cook, R. W., J. AGR. FOOD CHEM. 14, 430 (1966).
Farrow, R. P., Lamb, F. C., Cook, R. W., Kimball, J. R., Elkins, E. R., J. AGR. FOOD CHEM. 16, 65 (1968).
Finocchiaro, J. M., Benson, W. R., J. Assoc. Offic. Agr. Chemists 48, 736 (1965).
Guiffrida, Laura, J. Assoc. Offic. Agr. Chemists 47, 292 (1964).
Lamb, F. C., Farrow, R. P., Elkins, E. R., Cook, R. W., Kimball, J. R., J. AGR. FOOD CHEM. 16, 272 (1968).
Mills, P. A., J. Assoc. Offic. Agr. Chemists 42, 734 (1959).
Ott, D. E., Gunther, F. A., Residue Rev. 10, 70 (1965).
Ralls, J. W., Gilmore, D. R., Cortes, Antoni, J. AGR. FOOD CHEM. 14, 387 (1966).
Storherr, R. W., Watts, R. R., J. Assoc. Offic. Agr. Chemists 48, 1154 (1965).
U. S. Department of Agriculture, "USDA Summary of Registered Agricultural Pesticide Chemical Uses," 2nd ed., Pesticides Regulations Division, Agricultural Research Service, 1967.