

The Effect of Heat Processing and Storage on Pesticide Residues in Spinach and Apricots

Edgar R. Elkins,* Richard P. Farrow, and Eung S. Kim

Spinach and apricots were fortified separately with 15 commonly used pesticides representative of chlorinated hydrocarbons, organophosphates, and carbamate compounds. Fortified samples were analyzed before and after a representative heat treatment and after storage 1 year at ambient and 100°F temperatures. With the exception of Captan and Diazinon, pesticides in all three classes of compounds exhibited some degree of stability during the initial heat treatment given apricots. The heat treatment given apricots was less than that given spinach and this may be responsible for at least some

of the apparent stability. Under the storage conditions of the study, the carbamate pesticides appear to be quite stable in an acid product but not in low-acid product. Organophosphate pesticides were lost in both products tested, while chlorinated hydrocarbon stability seemed to depend on the compound itself. In nearly all cases, storage at 100°F for 1 year resulted in an additional loss of pesticide. In the case of the carbamate compounds, however, no additional loss was noted in apricots during these storage conditions.

The research reported in this paper may be considered a part of the extensive pesticide monitoring efforts now being carried out by federal agencies and private organizations. From sampling points throughout the United States, the Department of Agriculture and the Federal Water Quality Administration are compiling information on the levels of pesticide residues in the soil and in water systems. The "Market Basket" survey programs of the Food and Drug Administration provide an indication of the pesticide compounds that remain in food reaching the consumer. The objective of these efforts is to produce a reasonably detailed picture of what happens to pesticide residues in the environment, the rates with which they disappear from soils and water supplies, and the reactions that they may be expected to undergo while in the food chain.

Since commercially canned foods supply an important portion of the diet, no picture of the fate of pesticide residues in the environment and in the food chain can be complete without information on the effects of canning operations on permissible pesticide residues. It was the objective of this work to develop further information on the chemical changes occurring in residues of selected pesticide compounds during the processing and storage of canned fruits and vegetables.

Research carried out earlier revealed some rather surprising changes in 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane (DDT) and certain related residues during the processing of canned spinach. In this project it was learned that DDT is dechlorinated to 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane (TDE or DDD), and other compounds during the heat treatment required to commercially sterilize canned foods (Farrow *et al.*, 1966). The TDE may be decomposed by additional heating.

The work described in this paper is in the nature of a survey of the effects of thermal processing and storage on pesticide compounds. Selected food products were fortified with 15 pesticide compounds and, after being subjected to processing temperatures ordinarily encountered in canning, the fortified samples were analyzed for the original pesticide compound and any known breakdown products for which methods are available.

EXPERIMENTAL

Study of Thermal Processing Effects. Spinach and apricots were fortified separately with 15 commonly used pesticide

compounds. The samples were given representative heat processes and examined before and after processing, and after 1 year of storage at both 100°F and ambient temperatures. Ten to twelve No. 303 cans were processed for each pesticide-product combination. Unfortified lots of spinach and apricots were utilized as controls. The following pesticides were selected for study.

CHLORINATED HYDROCARBONS. Captan (*N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide); Lindane (γ -1,2,3,4,5,6-hexachlorocyclohexane); TDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane]; Thiodan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide); Toxaphene (chlorinated camphene); Methoxychlor [1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl) ethane].

PHOSPHATE COMPOUNDS. Diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate]; Guthion {*O,O*-dimethyl *S*-[4-oxo-1,2,3-benzotriazin-3(4*H*)-yl-methyl] phosphorodithioate}; Malathion {*S*-[1,2-bis(ethoxycarbonyl)ethyl]*O,O*-dimethyl phosphorodithioate}; Methyl parathion (*O,O*-dimethyl *O-p*-nitrophenyl phosphorothioate); Trithion {*S*-[[(*p*-chlorophenyl)thio]methyl]*O,O*-diethyl phosphorodithioate}.

CARBAMATE COMPOUNDS. Zineb (zinc ethylene bisdithiocarbamate); Ziram (zinc dimethyldithiocarbamate); Maneb (ethylenebisdithiocarbamate manganese); Carbaryl (1-naphthyl *N*-Methylcarbamate).

Samples from each lot of pesticide fortified spinach and apricots were analyzed after processing and the degree of thermal degradation of the pesticide compounds was determined. Additional cans were stored at ambient temperature and at 100°F and analyzed after 1 year of storage.

The thermal processing of pesticide fortified samples was standardized by using still retorting. The actual heat received by the contents of individual cans would thereby be within a narrow enough range to avoid wide variation in pesticide degradation due to variations in heat treatment. For each retort load used in sample preparation, five cans were monitored with thermocouples placed at the geometric center of the can. The processes selected for sample preparation were 65/66/252 for spinach and 65/50/217 for apricots where the numbers are initial temperature (°F), length of process in minutes, and processing temperature (°F), respectively.

The day before preparation of each pesticide fortified sample, one pail each of spinach and apricots was removed from frozen storage and allowed to thaw at room temperature for approximately 16 hr.

National Canners Association, Washington, D.C. 20036.

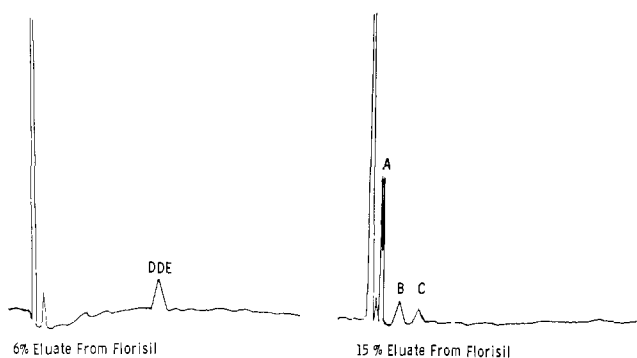


Figure 1. Gas chromatograms of unprocessed spinach control sample

For each pesticide-product combination the following sets of canned samples were prepared: thermally processed product plus pesticide; unprocessed product plus pesticide; thermally processed product; and unprocessed product. The unprocessed cans were frozen immediately after closing and were shipped and stored frozen until the analysis was started.

The product puree was fortified by adding a solution of the amount of pesticide required in approximately 10 ml of acetone to a 1-gal portion. The mixture was blended for 30 sec. The blended portion was added to the remainder of the puree to be used for a single day sample preparation and the mixture stirred manually with a paddle to insure uniform distribution of the pesticide.

The cans used were size 303 × 406 and were fully enameled with a coating developed for low pH products. They were filled manually to a weight of approximately 454 g and a normal headspace. The cans were closed and processed at the times and temperatures listed above.

After cooling and drying, the processed cans were divided into three lots: analyzed immediately; stored at ambient temperature for 1 year before analysis; and stored at 100°F for 1 year before analysis.

Control Analyses. In order that any gas chromatographic peaks arising from the processing of the fortified samples might be recognized and identified, considerable effort was devoted to the determination of "reagent blanks" and to the careful analysis of the control samples. The initial analytical work on the first control sample revealed the presence of several unidentified compounds in the cleaned-up sample presented to the gas chromatograph. When purified reagent grade solvents were carried through the entire analytical procedure as a "reagent blank," it was determined that the peaks were analytical artifacts. Subsequent work established that most of these were present in the Florisil used in the clean-up step and that they were due to the absorption of electron capturing compounds from the plastic liner used in packing the Florisil. Similar analytical artifacts can sometimes be obtained from sodium sulfate. When heat treatment failed to eliminate the peaks, a second batch of Florisil was obtained. The second batch also contained the electron capturing compounds but at a considerably lower level.

The results obtained from the analysis of the unprocessed spinach control sample are illustrated in Figure 1. The chromatogram shows both the 6 and 15% ethyl ether eluates from the Florisil clean-up column. The small peak in the 6% fraction was identified as *p,p'*-DDE at 0.02 ppm. The peaks labeled A and B appearing in the 15% ethyl ether fraction result from the Florisil as described above. The peak labeled C has not been identified.

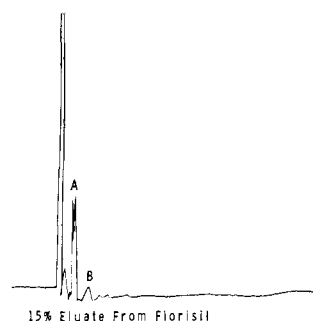


Figure 2. Gas chromatogram of Florisil reagent blank

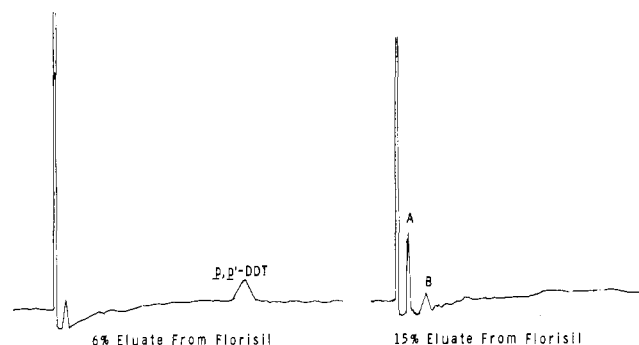


Figure 3. Gas chromatogram of unprocessed apricot control samples

Figure 2 illustrates a gas chromatogram of the 15% eluate of a "Florisil blank" obtained with the batch of Florisil which has been used for the analysis of the chlorinated hydrocarbon fortified samples. It has not been possible to eliminate the peaks arising from this source, however they do not interfere with the analyses.

The small amount of DDE appearing in the spinach control sample did not interfere in any of the analytical work. The analyses for the fortified processed and unprocessed samples are carried out at much lower levels of sensitivity and the peak does not appear in the chromatograms.

The control analyses of the apricots used for the fortification studies is illustrated in Figure 3. The peak present in the 6% eluate of this sample has been identified as *p,p'*-DDT at 0.12 ppm. The gas chromatographic identification has been confirmed by thin-layer chromatography. The Florisil artifacts also occur in the 15% eluate of this sample.

Analytical Methods. We rely primarily upon gas chromatographic procedures for the detection of chlorinated hydrocarbon pesticides and organophosphate pesticides. The extraction and clean-up methods are essentially those in widespread use in pesticide residue analyses (Food and Drug Administration, 1968).

Captan was extracted, cleaned-up, and determined by the official AOAC Method (Association of Official Analytical Chemists, 1965a).

The analysis of carbaryl was carried out according to the official AOAC Method (Association of Official Analytical Chemists, 1965b).

The analyses of maneb, zineb, and ziram were made using the procedure of Keppel (1969).

RESULTS AND DISCUSSION

To minimize any possible errors due to differences in purity of the pesticide reference materials used in this work, all

Table I. Effect of Heat Processing and Storage on Chlorinated Hydrocarbon, Organophosphate, and Carbamate Pesticides in Spinach and Apricots

| Pesticide | Percent reduction in residue level | | | | | | | |
|--------------------------|------------------------------------|-----------|--------------|------------|---------------------|-----------|--------------|------------|
| | Spinach | | | | Apricots | | | |
| | Initial, level ppm | Processed | Ambient 1 yr | 100°F 1 yr | Initial, level, ppm | Processed | Ambient 1 yr | 100°F 1 yr |
| Chlorinated hydrocarbons | | | | | | | | |
| Captan | 35.7 | 93 | 100 | 100 | 88.5 | 97 | 99 | 100 |
| Lindane | 10.1 | 33 | 49 | 99+ | 6.8 | 13 | 56 | 100 |
| TDE | 6.82 | 8 | 32 | 49 | 6.81 | 9 | 38 | 64 |
| Thiodan | 1.84 | 19 | 19 | 85 | 1.79 | 13 | 22 | 85 |
| Toxaphene | 6.5 | 27 | 60 | 95 | 6.8 | 7 | 35 | 92 |
| Methoxychlor | 12.6 | 21 | 65 | 100 | 12.5 | 0 | 82 | 100 |
| Organophosphate | | | | | | | | |
| Diazinon | 0.74 | 58 | 100 | 100 | 0.45 | 100 | 100 | 100 |
| Guthion | 1.2 | 100 | 100 | 100 | 1.00 | 61 | 100 | 100 |
| Malathion | 7.74 | 96 | 99+ | 100 | 7.63 | 32 | 84 | 100 |
| Methyl parathion | 0.88 | 100 | 100 | 100 | 0.85 | 54 | 100 | 100 |
| Trithion | 0.76 | 17 | 71 | 83 | 0.76 | 35 | 84 | 84 |
| Carbamate | | | | | | | | |
| Zineb | 6.8 | 100 | 100 | 100 | 6.7 | 20 | 42 | 48 |
| Ziram | 4.2 | 100 | 100 | 100 | 5.0 | 40 | 88 | 94 |
| Maneb | 9.9 | 100 | 100 | 100 | 9.8 | 40 | 53 | 54 |
| Carbaryl | 10.5 | 44 | 46 | 67 | 11.4 | 12 | 16 | 17 |

analytical reference standards were prepared from the same supply of pesticide chemicals utilized in the fortification of the canned samples. The chromatographic response of these pesticide compounds was also compared with that of identical compounds from independent sources.

Chlorinated Hydrocarbon Pesticides in Spinach and Apricots. The effect of thermal processing on thiodan residues in fruits and vegetables has not been studied. Maier-Bode (1968) has an excellent report on its properties, transformation products, and its effects on plants, but he does not discuss the effect of heat treatment on residues in fruits and vegetables. There is a closely related piece of work reported by McCaskey and Liska (1967) on thiodan in milk and milk products. When fed to milk cows, thiodan was metabolized to identifiable products that were almost totally found in the butter fat. Heat sterilization of condensed milk caused about a 25% reduction of thiodan sulfate.

Table I presents results obtained during this study on the changes in chlorinated compounds in spinach and apricots during processing and storage. The pureed products were fortified at or near their tolerance levels.

Examination of the spinach and apricot sample extracts produced no unidentified peaks on the chromatograms obtained after processing, or after storage at either temperature condition. Traces of the dehydrohalogenated TDE derivatives were obtained in both products. Thiodan sulfate does not appear in these chromatograms and was not obtained during this work. It is ordinarily seen in the analysis of field weathered samples.

The results indicate a decrease of 19% during processing of spinach and 13% during processing of apricots. There is little or no additional loss during storage at ambient temperatures for 1 year. Storage at elevated temperatures resulted in substantial decreases in thiodan in both spinach and apricots.

Thermal processing degrades captan almost completely and subsequent storage at ambient temperature results in further losses. The results of the present work are in agreement with the limited amount of information available in previous publications. Work done by Klayder (1963) indicated that captan is almost completely destroyed during processing of green

beans, asparagus, and spinach. For that study, captan was added to the vegetables at different levels and processed in mason jars. Beans and asparagus received heat treatments at 14 lb pressure for 35 min and spinach was heated under 15 lb pressure for 1 hr.

Captan is either degraded in spinach in the absence of heat or otherwise converted to forms not extractable by conventional methods. The pesticide was added at 100 ppm to both spinach and apricots. The unprocessed spinach samples averaged 36 ppm and the apricots 89.

Thermal processing resulted in a 93% decrease in the captan content of the fortified spinach, and a 97% decrease in apricots. After storage 1 year at ambient temperatures, captan was undetectable in spinach and only 1.1 ppm remained in apricots. Storage at elevated temperature for 1 year resulted in complete loss.

McCaskey and Liska (1967) reported that methoxychlor is unchanged during the heat treatment required for sterilization of condensed milk. In much earlier work utilizing colorimetric analytical methods, Brittin and Fairing (1950) reported that more than 90% was lost during the processing of peaches and pears. Our results suggest that the compound is relatively stable during thermal processing, but subject to degradation if heat is applied for a sufficient period. The heat treatment required for sterilization of condensed milk is mild compared to that utilized in the canning of some products. The heat treatment used by Brittin and Fairing was not specified.

The results indicate a 21% loss in processed spinach and no decrease during processing of apricots. However, ambient temperature storage evidently resulted in less degradation in spinach than in the more acid conditions present in the apricots. Storage at elevated temperatures resulted in a complete loss.

No unidentified peaks were obtained. The *p,p'*-methoxychlor olefin was identified in processed apricots stored for 1 year at both ambient and 100°F temperature conditions. This isomer was present at 0.17 ppm in the room temperature samples and at 0.19 ppm at 100°F. Only trace amounts were found in the corresponding spinach samples.

Lindane was added at 10 ppm, and the data presented in Table I indicate that the analyses of the unprocessed spinach samples resulted in virtually a "100% recovery," while the extraction from the unprocessed apricot samples may have been somewhat less effective. The pesticide is partially degraded during processing of both products, with the greatest apparent loss occurring in the spinach samples. A decrease of 33% was noted in the processed spinach and 13% occurred in apricots. The heat treatment for the spinach was somewhat more severe than that used for apricots and may account for the greater initial loss. During storage at room temperature, the decrease in the pesticide was approximately the same in both products. Loss of the pesticide in the samples stored at elevated temperatures was virtually complete in both spinach and apricots.

Langlois *et al.* (1964) reported that lindane residues were essentially stable during processing and storage of various dairy products under the conditions studied.

A very small amount of the α -BHC isomer, approximately 0.002 ppm in spinach and 0.007 ppm in apricots, was observed in gas chromatograms. This isomer was not observed in the chromatograms obtained from standard solutions of lindane prepared from the same supply of compounds utilized in the fortifications. Since the α isomer was present in such extremely small concentrations, the possibility of its formation during processing was not further investigated. No unexplained detector responses were obtained in the analyses of these samples. The complete degradation of lindane at the elevated storage temperature evidently resulted in end products not detected by conventional analytical methods for chlorinated hydrocarbons.

The conversion of DDT to TDE during heat processing of spinach has been reported (Farrow *et al.*, 1966). The further degradation of TDE was implied by some of the results obtained during that study, but it was not investigated in detail.

In the work reported here, spinach and apricots were fortified at 7 ppm with analytical grade *p,p'*-TDE. This material contained a small amount of *o,p'*-TDE, but it did not contain the dehydrohalogenated product *p,p'*-TDE olefin (TDE-HCl).

The total of the TDE isomers obtained in the unprocessed spinach and apricots closely approximated the fortification level. Processing reduced this level by approximately the same amount in both products, and ambient temperature storage resulted in a further loss, also nearly identical in both spinach and apricots. Elevated temperature storage resulted in a somewhat greater degradation in the apricots than in the spinach.

Evidently heat treatment resulted in the formation of small quantities of the TDE olefin in spinach and perhaps in apricots. The dehydrohalogenation of DDT and related compounds has been observed on some gas chromatographic columns. In our laboratory, columns are frequently checked with standard solutions to guard against the possibility that such analytical artifacts are being created. However, it is sometimes difficult to completely exclude this possibility. Traces of the dehydrohalogenated product were obtained in the unprocessed samples, and some conversion on the gas chromatographic column would account for this result. The larger quantities obtained in the spinach samples stored at elevated temperatures are primarily the result of conversion in the product during storage.

Traces of *p,p'*-DDE were observed in the chromatograms for the spinach, but these are present to about the same extent in the unprocessed control. The gas chromatograms for the

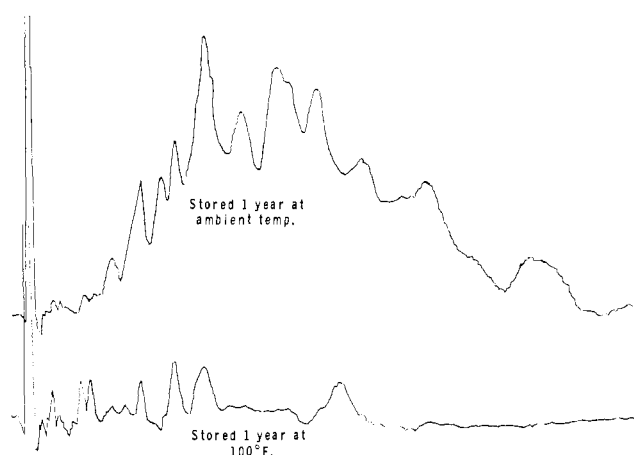


Figure 4. Gas chromatograms of toxaphene in processed spinach stored 1 year at ambient and 100°F temperatures

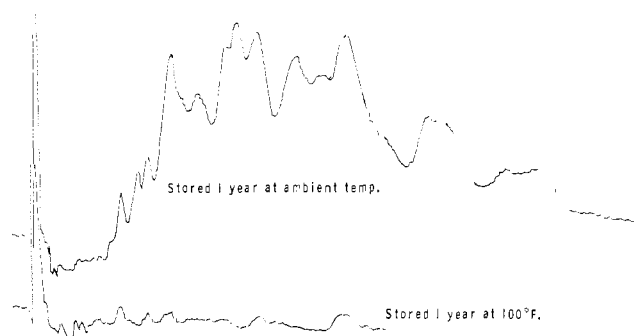


Figure 5. Gas chromatograms of toxaphene residues in processed apricots stored 1 year at ambient and 100°F temperatures

apricots stored at elevated temperatures also contain trace quantities of *p,p'*-DDE, but no indication of *p,p'*-DDT.

These results indicate that TDE is relatively stable during thermal processing of both spinach and apricots, although even ambient temperature storage for 1 year results in the degradation of a significant fraction of the original concentration.

Thompson and VanMiddeltem (1955) obtained information on the removal of toxaphene residues from vegetables by washing with and without the assistance of various surfactants. No information is available on the stability of this pesticide in fruits and vegetables during heat processing. The test samples in this study were fortified at 7 ppm, the tolerance level appropriate for both products at the time this work was started.

Quantitative data were obtained from the chromatograms by means of a disc integrater. Processing resulted in a somewhat greater decrease in spinach than in apricots. After storage at 100°F for 1 year, however, 90–95% of the pesticide had been degraded.

Figures 4 and 5 record illustrative chromatograms from the analyses of spinach and apricot samples at ambient and elevated temperatures. It is interesting to note that toxaphene chromatograms are somewhat altered by thermal processing or storage at elevated temperatures. The characteristic series of peaks obtained for this pesticide seem to appear in approximately the same order, but after heat treatment they are eluted much earlier. Some of the individual peaks may also be missing. Chromatograms of toxaphene in apricots appear somewhat changed, but not to the same de-

gree as those of the spinach samples. Any detailed study of the thermal degradation products of this pesticide would necessarily involve the use of a number of the isolated and purified major constituents of the mixture that constitutes the ordinary commercial pesticide material.

Organophosphate Pesticides in Spinach and Apricots. In contrast to many of the chlorinated hydrocarbon compounds, the organophosphate pesticides are regarded as relatively non-persistent. Ralls *et al.* (1966) reported the results of a study on the possible transformation products of diazinon after application to growing spinach, tomato, and green bean plants. Further work (Ralls *et al.*, 1967) covered the removal of this pesticide and its transformation products from tomatoes, spinach, and green beans during preparation for processing. The data obtained in this study are collected in Table I.

Diazinon was added to both spinach and apricots at a level of 0.75 ppm. This level was closely approximated by the results obtained on the unprocessed spinach controls; however, the unprocessed apricot controls averaged only 0.45 ppm. Evidently considerable portions of the added diazinon were degraded during and immediately following the fortification procedure. After processing, only barely detectable traces were present in the apricots. There had been a 58% decrease in the spinach sample. Storage at either ambient or elevated temperatures resulted in complete degradation of the added diazinon. There were no unknown peaks in any of the chromatograms of the diazinon fortified spinach or apricots.

Malathion was added at a level of 8 ppm, and this concentration was closely approximated in both the unprocessed apricot and spinach controls.

Malathion was more stable in apricots at pH 3.4 than in spinach, which has a pH of about 5.4. More than 96% of the pesticide was degraded in spinach during processing. The residue after 1 year at ambient temperature storage was almost undetectable, and at elevated temperatures no traces of the original compound remained.

In the apricot samples, only 32% of the added malathion was degraded during the processing step. After 1 year of ambient temperature storage, an additional 52% had disappeared, for a total loss of 84% due to processing and storage. Elevated temperature storage of the apricots resulted in virtually complete destruction. These results are in good agreement with those reported by Koivistoinen *et al.* (1964), who studied the fate of malathion residues in strawberries (47 to 58% loss), gooseberries (63%), plums (89%), tomatoes (16%), apples (90–96%), and green beans (98%). In comparing these figures, it should be kept in mind that processing temperatures and length of heat treatment are different in almost every case. Earlier work in these laboratories (Farrow *et al.*, 1968; Elkins *et al.*, 1968) indicates almost complete removal or destruction of malathion residues from tomatoes and green beans by commercial canning procedures.

No guthion residues could be found in spinach after heat processing and subsequent storage for 1 year at ambient and 100°F temperatures. In apricots a 61% loss of guthion was noted immediately after heat processing and no residue could be detected after a year's storage at the temperature indicated.

These results agree well with those reported by Carlin *et al.* (1966) who found almost complete removal of guthion from green beans during canning.

Methyl parathion is completely lost in spinach after processing. No residue could be detected in any of the storage samples. Our detection limit in this analysis is less than 0.005

ppm methyl parathion. The results on apricots suggest that methyl parathion is more stable in acid media, as only 54% of the original residue was lost during the heat treatment. The process given apricots, however, is less than that for spinach and the shorter heat treatment may contribute to this difference. Methyl parathion residue could not be detected in samples of apricots that had been stored 1 year at ambient and 100°F temperatures.

Spinach and apricots were fortified at 0.8 ppm trithion in these experiments. With the exception of the initial heat treatment, it exhibits about the same degree of loss in both products. Trithion also exhibits a degree of stability under these storage conditions, approximately 84% being lost in 1 year at 100°F. Gas chromatograms did not show unexplained peaks.

Carbamate Pesticides in Spinach and Apricots. Spinach and apricots were fortified with carbamate pesticides and given the respective processes outlined earlier. Results are shown in Table I. A significant amount of carbaryl was destroyed (44%) during the processing of spinach, but not in apricots (12%). Carbaryl apparently is more stable in acid type products such as apricots. Only 17% was destroyed during processing and subsequent storage at 100°F for 1 year. Sixty-seven percent of the carbaryl was destroyed in spinach due to this treatment. As mentioned earlier, the heat treatment given spinach is more rigorous than that given apricots and this probably plays an important role in the degree of destruction that takes place to these chemicals in any particular substrate. However, additional destruction or lack of it after the initial heat treatment may be related to the nature of the product. For example, no significant decrease of carbaryl is apparent after the initial loss of 12% due to processing, but an additional loss of 23% was noted in spinach due to storage at 100°F for 1 year.

Earlier work done at the National Canners Association and summarized by Farrow *et al.* (1969) seems to indicate more complete destruction of carbaryl in tomatoes, green beans, and spinach. However, this work reports removal by all canning operations and it must be taken into account that nearly all the residue removal took place prior to heat processing.

No maneb was found in spinach after the initial heat treatment. A 40% loss was realized in apricots after processing. An additional loss of 13 and 14% was noted after storage 1 year at ambient and 100°F temperatures, respectively. These results indicate that maneb may be relatively stable in acid products but readily degraded in low-acid foods during heat processing.

Maneb degrades to ethylene diamine and carbon disulfide or ethylene thiourea, carbon disulfide, and hydrogen sulfide. We did a headspace gas analysis on one can in each category but did not find CS₂ or H₂S in them. If these compounds had been present in the part-per-million range, we would have detected them.

No zineb residues were detected in spinach after the initial heat treatment was given. Only a 20% loss in apricots was realized after processing. A maximum residue loss of 54% was realized after processing, and subsequent storage for 1 year at 100°F. Zineb follows the same path of decomposition as maneb, yielding ether ethylene diamine and carbon disulfide or ethylenethiourea, carbon disulfide, and hydrogen sulfide. None of these products have been detected by our scheme of analysis.

No ziram residues were detected in spinach after processing. In apricots 40% of the residue was lost during heat treatment and storage for 1 year at 100°F temperature caused an addi-

tional 54% loss. Apparently ziram is not as stable in apricots during storage as maneb and zineb.

LITERATURE CITED

- Association of Official Analytical Chemists, "Official Methods of Analysis," 10th ed, 390 (1965a).
 Association of Official Analytical Chemists, "Official Methods of Analysis," 10th ed, 407 (1965b).
 Brittin, W. A., Fairing, J. D., *J. Ass. Offic. Anal. Chem.* **33**, 599 (1950).
 Carlin, A. F., Hibbs, E. T., Dahm, P. A., *Food Technol.* **20**, 80 (1966).
 Elkins, E. R., Lamb, F. C., Farrow, R. P., Cook, R. W., Kawai, M., Kimball, T. R., *J. AGR. FOOD CHEM.* **16**, 962 (1968).
 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).
 Farrow, R. P., Elkins, E. R., Rose, W. W., Lamb, F. C., Ralls, J. W., Mercer, W. A., *Residue Rev.* **29**, 73 (1969).
 Food and Drug Administration, *Pesticide Analytical Manual Vol. I*, 1968.
 Keppel, G. E., *J. Ass. Offic. Anal. Chem.* **52**, 162 (1969).
 Klayder, T. J., *J. Ass. Offic. Anal. Chem.* **46**, 241 (1963).
 Koivistoinen, P., Könönen, M., Karinpää, A., Roine, P., *J. AGR. FOOD CHEM.* **16**, 65 (1964).
 Langlois, B. E., Liska, B. J., Hill, D. L., *J. Milk Food Technol.* **27**, 264 (1964).
 Maier-Bode, H., *Residue Rev.* **22**, 1 (1968).
 McCaskey, T. A., Liska, B. J., *J. Dairy Sci.* **50**, 1991 (1967).
 Ralls, J. W., Gilmore, D. R., Cortes, A., *J. AGR. FOOD CHEM.* **14**, 387 (1966).
 Ralls, J. W., Gilmore, D. R., Cortes, A., Schutt, S. M., Mercer, W. A., *Food Technol.* **21**, 1030 (1967).
 Thompson, B. D., VanMiddel, C. H., *Amer. Soc. Horticult. Sci.* **65**, 357 (1955).
 Received for review May 24, 1971. Accepted August 23, 1971. Work conducted under contract No. 12-14-100-9513 (74) awarded to the National Canners Association Research Foundation by the Agricultural Research Service, U.S. Department of Agriculture. Presented before the Division of Agricultural and Food Chemistry, 161st Meeting, ACS, Los Angeles, California, March 1971.

Effects of Heating and Cooking Method on Chlorinated Hydrocarbon Residues in Chicken Tissues

S. J. Ritchey,* R. W. Young, and E. O. Essary

Lindane, endrin, heptachlor, dieldrin, and aldrin were fed at 10 ppm to broilers throughout an 8-week growing period. Tissues from these birds were cooked by baking, frying, or steaming and were heated in closed containers for 30-60 and 90 min. Residues, calculated on a dry matter basis, were lowered during cooking but the reduction in concentration was not significant in most cases. Lindane

concentration was reduced considerably when tissues were heated in closed containers. Heptachlor epoxide was lowered during heating, but the amounts of endrin, dieldrin, and aldrin were not reduced. Losses of these residues occurred primarily by leaching with fat and water, although there was some destruction of lindane and heptachlor epoxide by heating.

Previous work from this laboratory (Ritchey *et al.*, 1967, 1969) has demonstrated that DDT was broken into its isomers during the heating or cooking of chicken tissues. However, the concentration of the total amount of residue varied with the particular method of cooking. Dy *et al.* (1970) have recently followed the deposition of DDT and its isomers from the hen through the egg and into products containing eggs. The concentrations of residue in cakes were related to the amount of DDT in the eggs. Variations in the amounts of DDT in different types of cakes were related to the part of the egg utilized in preparation and the content of residue in that part.

Although a large number of reports, including those of Draper *et al.* (1950), Ivey *et al.* (1961), Liska *et al.* (1964), and Naber and Ware (1961), have indicated deposition of pesticide residues into chicken tissues, relatively few reports have examined the fate of residues during the cooking or heating of foods. The work of Liska *et al.* (1965, 1967) and Carlin *et al.* (1966) and those noted above are examples of efforts to define the effects of processing and preparation methods upon pesticide residues deposited in a wide variety of foods.

While DDT may represent the group of chlorinated hydrocarbons, the possibility that other residues of this general type may respond differently in the preparation of food seemed very good. Thus, the present report is concerned with the effects of cooking and heating on lindane, endrin, heptachlor, dieldrin, and aldrin present in chicken tissue.

EXPERIMENTAL PROCEDURE

Day-old Vantress AA male chicks were purchased from a commercial hatchery, housed in wire-screen batteries, and fed *ad libitum* commercial starter and grower rations to which had been added measured amounts of the pesticides. The only difference between groups of broilers was the pesticide added to the feed. Thirty chicks were randomly allotted to each treatment. They consumed feed containing the added pesticide throughout the 8-week growing period. Either lindane, heptachlor, endrin, dieldrin, or aldrin (10 ppm) was added to feed throughout the feeding period.

At the end of the growing period, birds were slaughtered, processed in the conventional manner, wrapped in freezer paper, and frozen at -20°F . The carcasses from each pesticide treatment were divided into equal numbers and were cooked or heated as described by Ritchey *et al.* (1969). Carcass weights of all birds were recorded and the amount of cooking loss was determined. The amounts of water and

*Departments of Human Nutrition and Foods, Biochemistry and Nutrition, and Food Science and Technology, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.