Disappearance of Malathion Residue in Broccoli during Cooking and Freezing

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A modified method for determining malathion [*O,O*-dimethyl *S*-(1,2 dicarbethoxyethyl) phosphorodithioate] residue in broccoli is described. Plants, harvested at intervals of one, two, three, and four days following malathion application, were washed and quartered. Opposite quarters were assayed immediately and the remaining two quarters analyzed after cooking or after six months' storage in the freezer. Broccoli plants showed mean losses after cooking of 9, 34, 8, and 7%, respectively, for plants harvested one, two, three, and four days after malathion applications. Raw plants harvested at the same intervals showed losses of 45, 69, 75, and 77%, respectively, after six months' storage in the freezer.

Malathion [*O,O*-dimethyl *S*-(1,2 dicarbethoxyethyl) phosphorodithioate] is widely used for control of pests on vegetable crops. The popular usage is based on its effective pesticidal qualities and fast disappearance rate which results in low residues in harvested vegetables (Koivistoinen, 1961; Speller, 1961).

The purpose of this experiment was to determine the residue levels resulting from sprays applied at different intervals before harvest and to determine to what extent the residues were removed by cooking or by storing at −9° C. for six months.

MATERIALS AND METHODS

A spring and fall crop of Spartan freezer broccoli plants were raised in the open field. The insecticide applied was Malathion 5-E, emulsifiable liquid, Woolfold Chemical Works, L & D, Fort Valley, Ga. The emulsifiable concentrated liquid was added to water according to directions on label of the container at a rate of 2.5 pounds to 100 gallons of water. The plants were sprayed weekly with a 3-gallon knapsack sprayer applying one gallon of spray to approximately a 60-foot row of broccoli plants. Plants were harvested at intervals of one, two, three, and four days following the malathion application. The harvested plants were washed thoroughly under running tap water and blotted dry with a paper towel. Then they were quartered with two opposite quarters assayed immediately and the other two quarters analyzed after cooking or after six months' storage in the freezer.

The broccoli was cooked by placing 1/2 cup of water in the sauce pan and adding 1/2 teaspoon of salt. The water was brought to a boil and 50 grams of broccoli were added immediately. The broccoli was covered and cooked for 5 minutes. Usually no liquor was left; if any liquor was left, it was measured for future calculations and included in the analysis.

Broccoli was blanched before freezing by heating in steam for five minutes. It was promptly chilled in ice water, packed in heavy plastic bags with little air space, and frozen at −9° C. for six months ± three days.

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Extraction and clean up procedures for subsequent gas chromatographic assays were modifications of methods of Mills (1961) and Mills *et al.* (1963). The procedure was modified as follows: Fifty grams of diced broccoli was used and reagents were reduced accordingly. No celite was used. After elution with 200 milliliters of 6% diethyl ether solution, column was immediately eluted with 400 milliliters of ether mixture (340 ml. of petroleum ether and 60 ml. of diethyl ether). The eluant was usually concentrated to 50 milliliters but sometimes to 25 or 100 in order to keep the sample in the straight line portion of the standard curve.

The petroleum ether and diethyl ether were prepared as described in a Guide to the Analysis of Pesticide Residues (U. S. Dept. of Health, Education, and Welfare, 1965). A gas chromatograph with an electron capture detector designed for pesticide analysis was used for the assays. The glass column was 6 feet × 1/4 inch and contained 2% OV-1 and 3% QF-1 on 100- to 200-mesh Chrom Q. The QF-1 is quite polar (Wilkens Instrument and Research, Inc.) while the OV-1 (Applied Science Laboratories) gives stability to the liquid phase.

Standard curves were prepared before and after each day's analysis and were in good agreement. The noticeable disadvantage in this method was that the detector had to be cleaned each week.

RESULTS AND DISCUSSION

This method used to detect malathion residues in broccoli resulted in good recoveries when amounts of malathion apt to be found in the sprayed malathion were added to the broccoli. Fifteen recoveries run intermittently during the experiment resulted in 92.2 ± 0.7% recoveries.

The amount of spray used was the dosage recommended by the Pesticides Regulation Division of USDA (1967), but the frequency of treatment was greater than any farmer would use. Still, at no time during either the fall or spring was the residue above tolerance (8 p.p.m.) after the three-day limitation period. In agreement with Koivistoinen *et al.*, 1964, the disappearance rate apparently was not affected by previous treatments. Any residue difference that might have been due to season was obliterated by differences that occurred when rains fell during the first 24 hours following application.

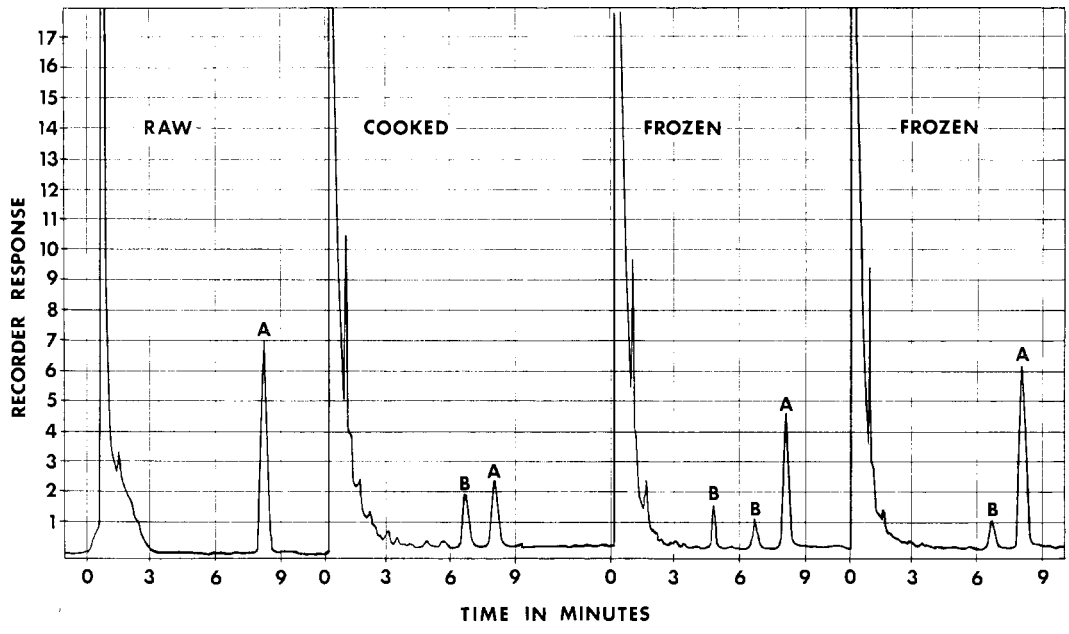

Figure 1. Typical gas chromatograms of raw, cooked, and frozen broccoli extracts

A. Malathion peaks
B. Unidentified peaks

Table I. Malathion Residues in Broccoli and Disappearance Rate during Cooking or Following Six Months' Storage in Freezer

	Days after Application			
	1	2	3	4
Mean residue in raw sample, p.p.m., 24 samples	10.3 ± 2.0	8.2 ± 2.3	5.4 ± 0.9	2.5 ± 1.3
Mean loss after cooking, %, 12 samples	9.0 ± 1.8	34.4 ± 3.0[a]	8.1 ± 1.9	7.2 ± 1.2[b]
Mean loss after freezing, %, 12 samples	45.4 ± 2.2	69.0 ± 3.7	75.3 ± 3.5	76.7 ± 3.6[b]

[a] Average of 7 samples, 5 assays that were 30% higher than mean were not used.
[b] Average of 9 samples; Other samples harvested on 4th day had only trace amounts of malathion and loss could not be measured.

Broccoli harvested one, two, three, and four days following application showed residues of 10.3 ± 2.0, 8.2 ± 2.3, 5.4 ± 0.9, and 4.5 ± 1.3 p.p.m., respectively.

Broccoli samples removed from the field one, two, three, and four days following application of malathion showed losses of 9.0 ± 1.8, 34 ± 3.0, 8.1 ± 1.9, 7.2 ± 1.2%, respectively, after cooking. The large loss on the second day may reflect the fact that this is at the time when the disappearance rate in the field is relatively high. Broccoli harvested from one to four days after application of malathion showed disappearance rates varying from 36 to 90% after storing in freezer at −9° C. for six months. Plants harvested one, two, three, and four days after spraying showed average losses of 45.4 ± 2.2, 69.0 ± 3.7, 75.3 ± 3.5, and 76.7 ± 3.6%, respectively, after six months' storage in the freezer. The increase in disappearance rate with increasing interval between spraying and harvesting would suggest that some type of degradation occurs in the growing plant that facilitates degradation during freezing.

Malathion residues were below tolerance (8 p.p.m.) after freezing in plants picked as early as the second day following application. Unidentified peaks that were not present in the raw broccoli occurred in both the cooked and frozen broccoli. Good examples of the unidentified peaks may be seen in the typical chromatograms presented in Figure 1. All cooked or all frozen samples did not exhibit these peaks. The peak with a retention time of 6½ minutes appeared in about 30% of the cooked broccoli chromatograms and in over 75% of the frozen broccoli chromatograms.

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