

DEGRADATION OF CAPTAN RESIDUES
ON STRAWBERRY AND GRAPE FOLIAGE
IN CALIFORNIA

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SUMMARY

Six strawberry fields in Monterey and Orange Counties and nine grape vineyards in Stanislaus and Tulare Counties, California, were monitored for dislodgeable foliar residues of captan during May through August, 1987. The data were employed to characterize the initial deposition and foliar residues of captan, and where possible, estimate decay rates. Triplicate leaf disc samples were collected from each field or vineyard at varying intervals over 14 to 42 days post-application and analyzed for captan residues.

The information gathered for this report will be used to aid in estimating human exposures in captan risk assessment.

INTRODUCTION

This study was conducted to determine and characterize initial deposition and/or decay rates of captan on strawberry and grape foliage. The information will be used to aid in estimating human exposure to captan. This exposure estimate, along with dermal absorption and the metabolic fate of captan, will be used to develop a human risk assessment of captan.

The study was initiated when captan was identified by a registrant-submitted chronic feeding study as having adverse effects in mice. The adverse effect of major concern was an oncogenic effect in mouse gastro-intestinal mucosa, indicated by mouse oncogenicity studies from Stauffer Environmental Health Center (1) and Chevron Environmental Health Center (2).

Captan (cis N[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide) is an off-white powder that is insoluble in water and moderately soluble in organic solvents. In dry conditions it is stable, but degrades rapidly in water or alkaline environments. It has a very low acute toxic potency with an oral LD₅₀<rat> of 9,000 mg/kg and a dermal LD₅₀<rabbit> of 7,500 mg/kg (3).

Captan is a broad spectrum protectant-eradicator fungicide. It is used in grapes to control dead arm, downy mildew and black rot, and to control botrytis rot and other fungus diseases in strawberries. It is typically applied on grapes one to three times per season. Captan is typically applied on strawberries every two to four weeks throughout the season, but can be applied weekly if necessary. The reentry interval is four days for all crops.

MATERIALS AND METHODS

With the assistance of the County Agriculture Commissioners in Monterey, Orange, Stanislaus and Tulare Counties, six strawberry fields and nine grape vineyards were selected and monitored for a period of two to six weeks.

APPLICATION INFORMATION

Strawberries

All applications were made by conventional ground sprayers, using Captan 50 percent wettable powder at a delivery rate of four pounds [REDACTED] per acre. Applications were scheduled every two to four weeks throughout the season. The strawberry fields were harvested twice per week, from approximately March through October, depending on local weather conditions.

Grapes

All eight Tulare County vineyard captan treatments were applied by conventional air-blast sprayers or vineyard dusters. Six of the vineyards (fields 30-38) were treated with Captan Dust at the rate of two pounds active ingredient per acre. Two of the vineyards (fields 39 and 40) were treated with captan 50 percent wettable powder at the rate of 1.5 pounds active ingredient per acre. In Stanislaus County (field 25), an electrostatic sprayer was used to apply Captan 50 percent wettable powder at the rate of 2.5 pounds active ingredient per acre. All treatments were applied approximately one month prior to harvest.

SAMPLING TECHNIQUES

Fields were evaluated using a sampling strategy adapted from the methods of Iwata, et al. (4), according to the following scheme:

Each field was divided into three sections with one row selected from each section. The sample areas were selected to approximate a diagonal across the field. The rows were marked with flagging tape. Fifteen to 20 foliage disc samples were collected from each row using a Birkestrand leaf punch, 2.5 centimeters in diameter, fitted with a four ounce jar. The leaves sampled were those most likely to be contacted by a worker hand-harvesting the crop, i.e., the outer leaves or top leaves. One complete sample consisted of 15-20 foliage discs from each of the three sampling areas for a total of 45-60 foliage discs per field. The number of foliage discs collected from each field was recorded and used to calculate total surface area of each sample. Three replicate samples were collected from each field. The jar containing each sample was sealed with aluminum foil, capped, and stored immediately on ice. Samples were shipped to (CDFA) Chemistry Laboratory Services in Sacramento for residue extraction within 24 hours.

SAMPLING SCHEDULE

Pre-application samples were collected on the day of application for all strawberry fields. No pre-application samples were available for any of the grape vineyards, as all the cooperators had applied their final captan treatments of the season when the study was initiated.

Post-application samples were collected at varying intervals from each field, but included 24 hours, two days, and approximately one week, two weeks, three weeks and four weeks post-application. Sampling was conducted on strawberries during May and June, 1987. Grape sampling was conducted during July and August, 1987.

ANALYSIS OF SAMPLES

Each foliage sample was analyzed by the Chemistry Laboratory (CDFA) for dislodgeable residue of captan within 48 hours of receipt. Residues were rinsed from the leaf surface using a water-surfactant solution, then extracted from the aqueous solution with ethyl acetate. Analysis was by gas chromatography. The limit of detection was 0.0005 micrograms per square centimeter of leaf surface.

STATISTICAL METHODS (5)(6)(7)

Nonlinear iterative least square regression techniques were employed to examine both initial deposition and decay rates in the study. Initial analysis assumed a first-order exponential decay model which takes the following functional form:

$$Y = f(t) = B_0 e^{-B_1 t_1}$$

where B_0 = initial deposition
 B_1 = decay rate
and t = time since application

Comparisons of decay rate and initial deposition estimates were made by t-tests using the weighted asymptotic estimates of the standard deviation. Parallel analyses using the logarithmic transformed linearized regression were also conducted.

RESULTS

Strawberry Foliage

One strawberry field in Monterey and five in Orange County were monitored over a four week period. Pre-application foliar captan residues ranged from 0.004 ug/cm² to 0.430 ug/cm². At 24 hours post-application, the concentration of captan on leaf surfaces ranged from 0.965 ug/cm² to 4.29 ug/cm². At 14 days post-application, four of the six fields monitored had foliar residues below 0.10 ug/cm². Residues for all fields were below 0.10 ug/cm² at 21 days. Residue data are presented in Table 1 and Figure 1. Captan residues follow a first order exponential curve. The plot in Figure 1 indicates a range of expected foliar captan residues at post-application intervals.

Grape Foliage

Eight grape vineyards in Tulare County and one vineyard in Stanislaus County were monitored over a four week period. The initial sampling took place between eight hours and 25 days post-application. Interval sampling continued for 28 to 42 days post-application. No pre-application samples were available. For all Captan Dust applications (Fields 30-38), the residues at all sampling intervals were below 0.5 ug/cm² (See Table 3 and Figure 2). For the two fields treated with Captan 50 percent wettable

powder (Fields 39 and 40), the concentration of captan residues on leaf surfaces ranged from 0.54 ug/cm² to 2.00 ug/cm². At one week post-application, foliar residues ranged from 0.10 ug/cm² to 1.5 ug/cm². All Tulare County fields had captan foliar residues of less than 0.1 ug/cm² at 21 days post-application (See Table 3 and Figure 3). The Stanislaus County vineyard (Field 25) was treated via electrostatic sprayer. The concentration of captan residues on the leaf surfaces in this vineyard was much higher than residues found in the Tulare County fields. At 21 days post-application, when all other fields had residues below 0.1 ug/cm², Field 25 had foliar residues averaging 4.3 ug/cm². At 42 days post-application, Field 25 had mean residue concentrations of 1.8 ug/cm². Tabular and graphical presentations of residue data are shown in Table 3 and Figures 2 through 4.

Decay Rates

Decay rates were estimated for each strawberry field. The estimated decay rates ranged from 0.06 to 0.19. The estimated decay rates accounted for 83 percent to 93 percent of the expected variation. The summary of regression analysis is presented in Table 2. The grape residue data did not lend itself to statistical analysis because, without pre-application samples, it is impossible to estimate the captan residue present from previous applications in the season.

DISCUSSION

Strawberries

Captan was applied to strawberries at two to four week intervals throughout the season. This schedule allowed for sampling to be arranged to include pre-samples of the strawberry foliage. These samples, taken the day before a captan application, quantified the amount of captan remaining on the leaf surfaces from previous applications. This amount was subtracted from the residue levels found on the foliage at the first post-application sampling, so that a determination of initial deposition could be made. The degradation and dissipation of the amount of captan initially deposited were then evaluated at intervals over two to four weeks, until the subsequent captan application. This information can be used in preliminary estimates of human exposure risks.

Grapes

The captan applications to grapes were made one to three times during the season. At the time this study was initiated, all captan treatments were completed for the season. Therefore, no pre-samples were available and no determination of initial deposition could be made for grape foliage. The data obtained is useful as background information only. Further study, including pre-application sampling, is necessary before decay rates or risk estimates can be determined.

Field 25 was the only vineyard where captan was applied by electrostatic sprayer. The residues appeared to behave differently in this vineyard than

residues from vineyards where the captan applications were by conventional ground rig. Captan was applied to Field 25 at the rate of 2.5 pounds active ingredient per acre, which represents a 25 to 60 percent increase over the captan treatments for the eight Tulare County fields. At 21 days, the residues on foliage after the electrostatic application were 5 to 215 times greater than any of the foliage residues from the other 8 grape vineyards. At 42 days post-application, the mean concentrations of residues after the electrostatic application were 12 to 225 times greater than the mean for any other vineyard monitored (see Table 3 and Figure 4). Since residue data from an electrostatic sprayer application is available for only one field, it is unclear whether use of this type of spray equipment would generally result in increased deposition on leaf surfaces, or if the increased deposition was due solely to the increased amount of captan applied to this field. This phenomenon needs to be investigated and characterized further. This Branch is currently planning to conduct a pilot study of electrostatic and other low volume spray applications during the summer of 1989. We hope to determine and quantify any significant differences in pesticide residues resulting from electrostatic sprayer applications at that time.

CONCLUSION

The data obtained from analysis of strawberry foliage for captan residues were sufficient to determine and characterize initial deposition and decay rates. This information can be used in estimating human exposure to captan. The data obtained from analysis of grape foliage for captan residues were insufficient to determine and characterize initial deposition and decay rates. Further investigation is needed before human exposure estimates can be made. Specifically, pre-application sampling and an examination and assessment of the characteristics of various types of spray equipment commonly used to apply captan to grapes are needed to estimate human exposures in the captan risk assessment.

TABLE 1

Foliar Dislodgeable Residues for Captan on Strawberries
 Data From Samples Taken May Through June 1987
 (All Residues Shown in Micrograms Per Square Centimeter)

<u>County</u>	<u>Field Number</u>	<u>Sampling Interval</u>	Replicate <u>a</u>	Replicate <u>b</u>	Replicate <u>c</u>	<u>Mean</u>	<u>Std Dev</u>
Monterey	1	Pre-application	NS	NS	NS		
		8 Hours	4.19	2.96	2.87	3.34	0.74
		Day 1	2.87	3.86	4.29	3.37	0.70
		Day 2	2.81	4.09	3.97	3.62	0.71
		Day 7	2.47	2.04	2.37	2.29	0.23
		Day 9	2.02	2.12	2.18	2.11	0.08
		Day 16	1.20	1.48	1.26	1.31	0.15
		Day 21	0.87	0.80	0.95	0.87	0.08
		Day 28	1.30	0.73	1.26	1.10	0.32
Orange	10	Pre-application	0.00	0.01	0.00	0.00	0.00
		2 Hours	4.78	4.51	4.86	4.72	0.18
		Day 1	3.14	3.17	3.50	1.32	0.58
		Day 7	0.94	2.80	1.04	0.98	0.11
		Day 14	1.07	1.02	0.85	0.43	0.05
		Day 22	0.47	0.38	0.43		
Orange	20	Pre-application	0.01	0.01	0.01	0.01	0
		2 Hours	3.22	2.96	2.82	3.00	0.20
		Day 1	0.96	1.72	1.81	1.50	0.47
		Day 7	0.80	0.06	0.51	0.46	0.37
		Day 14	0.69	0.53	0.82	0.68	0.15
		Day 21	0.16	0.22	0.18	0.19	0.03
		Day 28	0.05	0.40	0.08	0.18	0.19
Orange	40	Pre-application	0.01	0.01	0.02	0.02	0.01
		2 Hours	2.86	1.81	2.00	2.22	0.56
		Day 1	1.42	1.42	1.81	1.55	0.26
		Day 7	0.61	0.96	0.89	0.82	0.19
		Day 13	0.33	0.38	0.21	0.31	0.09
		Day 21	0.03	0.50	0.05	0.04	0.01
		Day 28	0.02	0.01	0.01	0.01	0.00
Orange	80	Pre-application	0.02	0.01	0.007	0.02	0.00
		2 Hours	2.49	3.63	2.780	2.97	0.59
		Day 1	3.69	3.01	3.480	3.39	0.35
		Day 7	1.61	1.35	2.040	1.67	0.35
		Day 14	0.41	0.44	0.440	0.43	0.02
Orange	81	Pre-application	0.43	0.32	0.310	0.35	0.07
		6 Hours	1.87	2.27	2.750	2.30	0.44
		Day 1	2.53	2.06	1.860	2.15	0.34
		Day 7	0.92	0.68	0.960	0.85	0.15
		Day 14	0.50	0.44	0.510	0.48	0.04
		Day 21	0.33	0.34	0.320	0.33	0.01

ND - None detected, below 0.0005 ug/cm², minimum detectable level.
 NS - No sample taken.

TABLE 2

Summary of Regression Analyses for
Captan Foliar Degradation on Strawberries

<u>Field</u>	<u>Initial Deposition ug/cm²</u>	<u>First Order Decay Rate (mg/cm²/day)</u>	<u>R Squared</u>
	Estimate	Estimate	Estimate
1	3.70	0.06	0.89
10	4.33	0.15	0.92
20	2.54	0.19	0.83
40	2.07	0.15	0.91
80	3.36	0.11	0.88
80	2.40	0.12	0.93

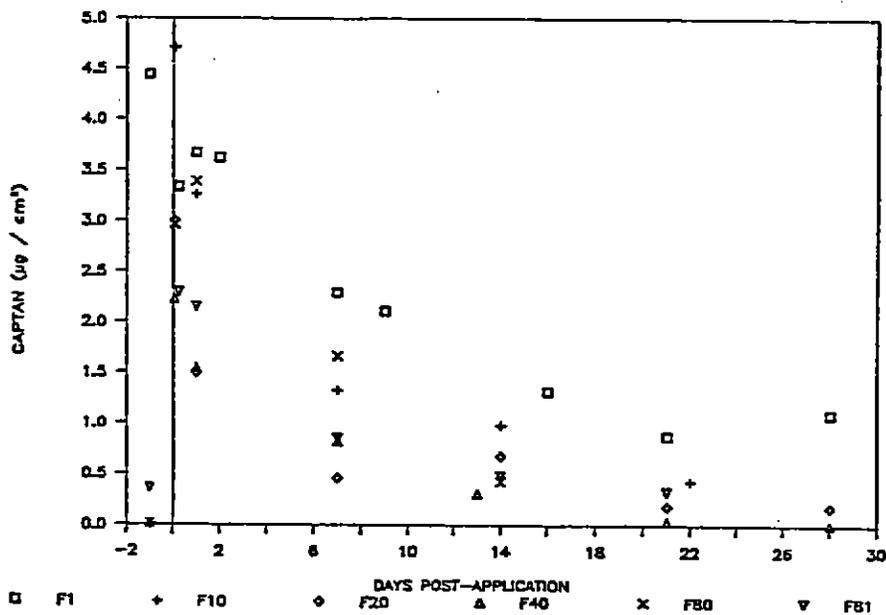


Figure 1. Foliar residues on strawberries. Fields treated with captan 50 WP at 4 pounds per acre.

TABLE 3

Dislodgeable Foliar Residues for Captan on Grapes
(Residues Shown in Micrograms Per Square Centimeter)

Field Number	Day Post-Application	Replicates			Mean	Std. Dev
		a	b	c		
30	21	0.14	0.16	0.15	0.15	0.01
	28	0.06	0.06	0.04	0.05	0.01
	35	0.03	0.03	0.05	0.04	0.01
	42	0.02	0.07	0.07	0.05	0.03
31	21	0.43	0.30	0.35	0.36	0.07
	28	0.20	0.17	0.16	0.18	0.02
	35	0.30	0.21	0.28	0.26	0.05
	42	0.14	0.16	0.17	0.16	0.02
33	25	0.02	0.02	0.02	0.02	0
	30	0.01	0.02	0.01	0.01	0
	36	0.03	0.02	0.02	0.02	0
	42	0.01	0.01	0.01	0.01	0
34	25	0.003	0.01	0.01	0.00	0
	30	0.01	0.01	0.01	0.01	0
	36	ND	ND	ND	-	-
	42	0.004	0.01	0.01	0	0
36	7	0.05	0.04	0.04	0.04	0
	14	0.02	0.04	0.03	0.03	0.01
	21	0.02	0.02	0.02	0.02	0
	28	0.03	0.03	0.03	0.03	0
38	7	0.10	0.12	0.15	0.12	0.03
	14	0.09	0.12	0.11	0.11	0.02
	21	0.03	0.03	0.03	0.03	0
	28	0.04	0.07	0.07	0.06	0.02
39	8 Hours	1.6	1.6	2.0	1.73	0.23
	7	1.3	1.5	1.1	1.30	0.20
	14	0.72	1.0	1.0	0.91	0.16
	21	0.81	0.78	0.42	0.67	0.22
	28	0.14	0.24	0.10	0.16	0.07
40	8 Hours	0.67	0.54	1.1	0.77	0.29
	7	1.1	1.5	1.5	1.37	0.23
	14	1.4	1.7	1.3	1.47	0.21
	21	0.50	0.65	0.69	0.61	0.10
	28	0.70	0.76	0.90	0.79	0.10
25	21	4.2	4.4	4.4	4.33	0.12
	28	2.9	2.6	3.4	2.97	0.40
	35	1.6	2.5	3.7	2.60	1.05
	42	1.5	1.2	2.8	1.83	0.85

ND - None detected. Residues below MDL of 5×10^{-4} ug/cm²

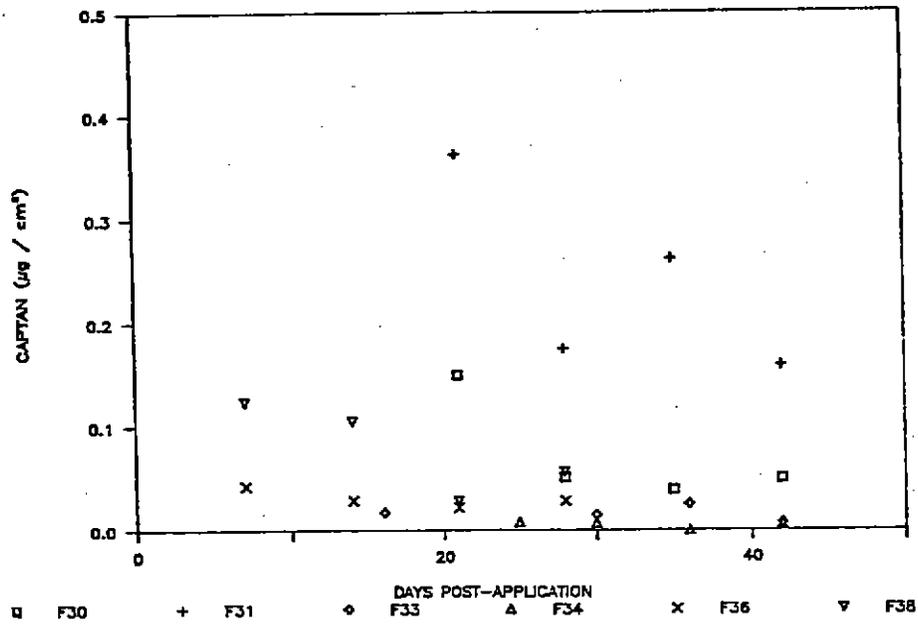


Figure 2. Foliar residues on grapes. Fields treated with captan dust at 2 pounds per acre.

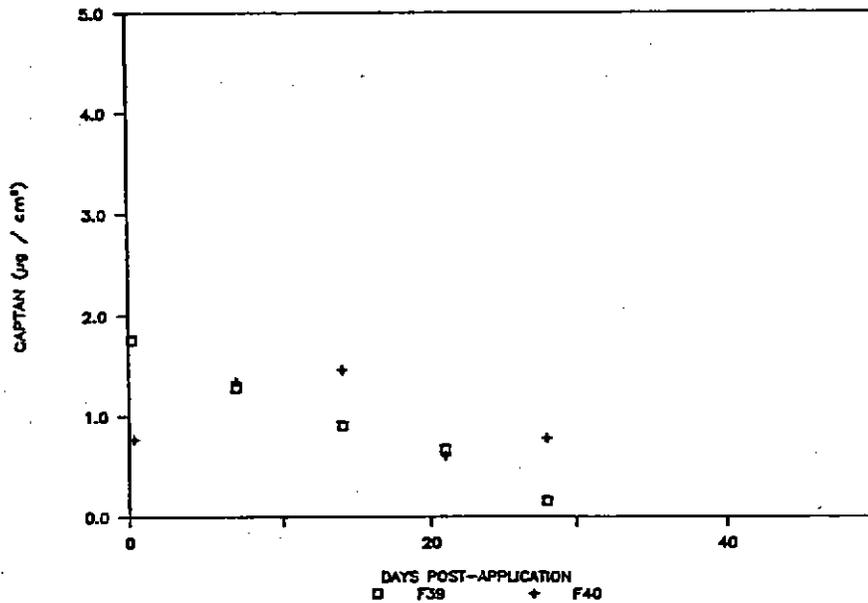


Figure 3. Foliar residues on grapes. Fields treated with captan 50 WP at 1.5 pounds per acre.

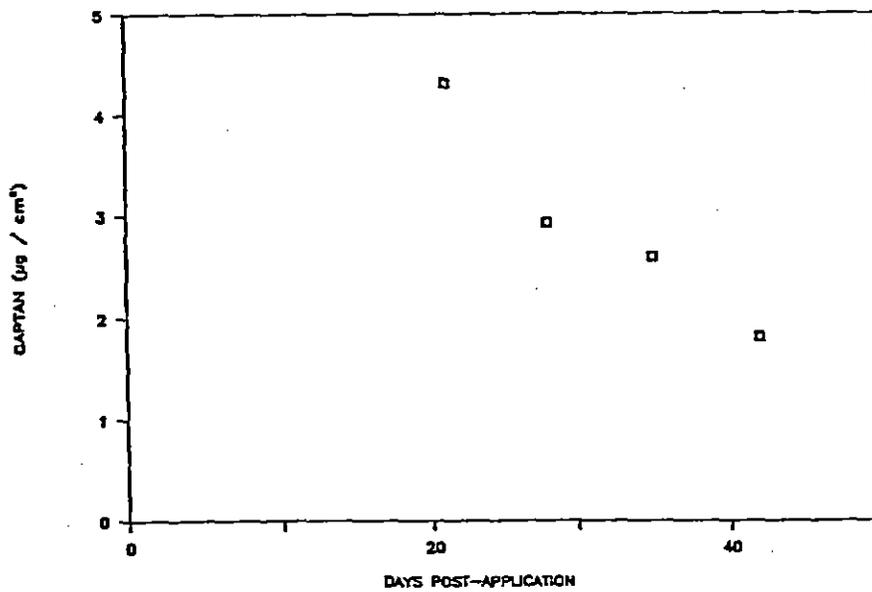


Figure 4. Foliar residues on grapes. Field treated with captan 50 WP at 2.5 pounds per acre, applied by electrostatic sprayer.

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APPENDIX I

CAPTAN

This method is for the determination of dislodgeable Captan residues from leaf surfaces.

ANALYSIS:

1. Add 50 mls of distilled water and 0.2 ml Sur-ten solution to the jar containing the leaf punches.
2. Rotate the jar for 20 minutes.
3. Decant the aqueous solution into a separatory funnel.
4. Repeat steps 1-3 twice more.
5. Add 50 grams of NaCl to the sep. funnel and shake to dissolve.
6. Extract the aqueous solution with 50 mls of Ethyl Acetate, draining the solvent through glass wool and Na₂SO₄ into a graduated cylinder.
7. Extract the aqueous solution twice more with 25 mls of Ethyl Acetate, combining all extracts in the same cylinder.
8. Bring the final volume in the cylinder up to 100 mls.

Gas chromatograph - HP 5880A.

Oven temperature - 195 C.

Injector temperature - 225 C.

Detector temperature - 350 C.

For capillary configuration:

Column pressure - 15 PSI.

Split vent - 50 mls/min.

Septum purge - 2 mls/min.

ECD make-up gas flow - 30 mls/min.

Using these conditions, Captan has a retention time of 5.63 minutes.

Results are reported as micrograms of Captan per square centimeter per sample.

Recovery: 10 ugs Captan - 98%