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STABILITY OF RESIDUES OF METALAXYL AND ITS METABOLITES UNDER FREEZER STORAGE CONDITIONS

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A freezer storage stability study was conducted to demonstrate the validity of analytical results obtained by determination of residues of metalaxyl and its metabolites in tobacco and potato samples. Cured tobacco and potato samples fortified with metalaxyl and stored at 5°F were analyzed for the parent compound over a twelve-month period. No loss of metalaxyl occurred in either substrate during this period.

Field-treated cured tobacco and potato samples analyzed for combined residues of metalaxyl and its metabolites which are converted to 2,6-dimethylaniline by refluxing phosphoric acid were reanalyzed for the combined residues after 18 months of freezer storage. No loss of determinable residues occurred during this period in either substrate.

These results demonstrate the stability of parent metalaxyl residues for at least 12 months and combined residues of parent and metabolites for at least 18 months under the freezer conditions employed.

INTRODUCTION

The stability of pesticides in stored samples is important in developing meaningful residue data. The stability of metalaxyl (CGA-48988) and its metabolites which are converted to 2,6-dimethylaniline by phosphoric acid reflux was investigated. Tobacco and potato samples fortified in the laboratory with metalaxyl were stored (5°F) and analyzed for metalaxyl at several intervals over a twelve-month period. Additionally, field-treated samples were analyzed for combined residues of metalaxyl and its metabolites containing the 2,6-dimethylaniline moiety in November 1978 and again in May 1980 after storage in the freezer.

EXPERIMENTAL

Preparation of Fortified Samples for Freezer Storage: Samples of chopped control cured tobacco were fortified with 5 ppm of metalaxyl using an acetone stock solution. Similarly, chopped control potatoes were fortified with 0.2 ppm of metalaxyl. The solvent was allowed to evaporate and the samples were stored in glass jars in a freezer at 5°F. Unfortified control samples were similarly frozen.

A control sample, a freshly fortified control sample (5 ppm for tobacco and 0.2 ppm for potatoes), and a stored fortified sample were analyzed for metalaxyl at 0-day, and after 1, 2, 4, 6, and 12 months of storage.

Field-treated samples of cured tobacco (AG-A 4732) and potatoes (AG-A 4935) were chopped and analyzed in November 1978 for combined residues of metalaxyl and its metabolites containing the 2,6-dimethylaniline moiety. These samples, which contained finite residues, were stored in plastic bags in a freezer at 5°F under normal conditions for retaining residue samples. These samples were reanalyzed for the combined residues after 18 months of storage.

Analytical Methodology: Parent metalaxyl residues in tobacco and potato samples were determined according to Analytical Method AG-325. According to this method, residues of metalaxyl are extracted from crop samples by blending with 20% water in methanol for 10 minutes. An aliquot of the extract is evaporated, acidified and

partitioned with dichloromethane. The organic phase is evaporated to dryness and cleaned up by chromatography on a Grade V alumina column. Final determination is made using a gas chromatograph equipped with an alkali flame ionization detector operating in the nitrogen-specific mode.

Combined residues of metalaxyl and its metabolites containing the 2,6-dimethylaniline moiety were determined according to Analytical Method AG-330. This method involves an initial extraction by blending with 20% water in methanol. An aliquot of the extract is evaporated, then refluxed with phosphoric acid overnight in the presence of cobalt chloride. The solution is basified and the 2,6-dimethylaniline formed is steam distilled. The product is derivatized with trichloroacetyl chloride to minimize the problems of volatility of the aniline. The derivative is cleaned up by alumina column chromatography and analyzed by gas chromatography using an alkali flame ionization detector operating in the nitrogen-specific mode. Results are reported as ppm equivalents of metalaxyl.

RESULTS AND DISCUSSION

Results of the analyses of the stored fortified samples are given in Table I for tobacco and Table II for potatoes. The recoveries of metalaxyl in the stored fortified samples averaged 103 ± 4% in tobacco and 100 ± 16% in potatoes. These values are comparable to the recoveries found in the freshly fortified samples: 89 ± 9% for tobacco and 101 ± 12% for potatoes. No depletion of residues was observed in the 12-month study period.

The results of the determinations of the combined residues of metalaxyl and its metabolites determined as 2,6-dimethylaniline in field-treated tobacco and potatoes are given in Table III. No loss of combined residues was observed in either tobacco or potatoes after an 18-month storage period.

CONCLUSION

Residues of parent metalaxyl in cured tobacco and potatoes are stable for at least 12 months when stored in a freezer at 5°F. Combined residues of metalaxyl and its metabolites determined as 2,6-dimethylaniline in tobacco and potatoes are stable for at least 18 months under these storage conditions.

TABLE I: DETERMINATION OF PARENT METALAXYL IN CONTROL AND FORTIFIED CURED TOBACCO FOLLOWING FREEZER STORAGE (5°F)

Storage Interval	Unfortified Control ppm Found	Control Freshly Fortified - 5 ppm ppm Found[a]	Control Freshly Fortified - 5 ppm Percent Recovery	Stored Fortified Sample - 5 ppm ppm Found[a]	Stored Fortified Sample - 5 ppm Percent Recovery
0 days	<1.0	4.1	82%	5.1	103%
1 month	<1.0	4.2	83%	4.9	98%
2 months	<1.0	4.4	89%	5.4	107%
4 months	<1.0	4.1[b]	81%	5.2	104%
6 months	<1.0	5.0	100%	4.9	99%
12 months	<1.0	5.1	101%	5.4	108%
Average ± std. dev.			89 ± 9%		103 ± 4%

[a]Determined according to AG-325.

[b]Control sample freshly fortified with 0.5 ppm of metalaxyl.

TABLE II: DETERMINATION OF PARENT METALAXYL IN CONTROL AND FORTIFIED POTATOES FOLLOWING FREEZER STORAGE (5°F)

Storage Interval	Unfortified Control ppm Found	Control Freshly Fortified - 0.2 ppm ppm Found	Control Freshly Fortified - 0.2 ppm Percent Recovery	Stored Fortified Sample - 0.2 ppm ppm Found	Stored Fortified Sample - 0.2 ppm Percent Recovery
0 days	<0.05	0.16	80%	0.14	71%
1 month	<0.05	0.22	108%	0.20	102%
2 months	<0.05	0.23	116%	0.23	115%
4 months	<0.05	0.21	104%	0.21	103%
6 months	<0.05	0.20	98%	0.23	114%
12 months	<0.05	0.20	100%	0.19	95%
Average ± std. dev.			101 ± 12%		100 ± 16%

TABLE III: DETERMINATION OF COMBINED RESIDUES OF METALAXYL AND ITS METABOLITES AS 2,6-DIMETHYLANILINE IN FIELD-TREATED CURED TOBACCO AND POTATOES FOLLOWING 18 MONTHS OF FREEZER STORAGE (5°F)

Crop	Sample No.	Application Rate (lb. ai/A)	First Analysis Date	First Analysis ppm Found[a]	Second Analysis Date	Second Analysis ppm Found[a]
Cured Tobacco AG-A 4732 II 84-day PHI	3A	3	10/25/78	83	5/28/80	85, 87, 87[b]
	4A	6	10/25/78	128	5/9/80	152
Potatoes AG-A 4935 1-day PHI	1C	0.5	11/12/78	0.15	5/9/80	0.16
	1D	0.5	11/12/78	0.15	5/9/80	0.16
	1E	1	11/12/78	0.16	5/9/80	0.17
	1F	1	11/12/78	0.13	5/9/80	0.13

[a]Determined according to AG-330.

[b]Sample was analyzed using triplicate subsamples.