SOME SUGGESTIONS FOR STUDYING THE ENVIRONMENTAL CHEMISTRY OF CARBOFURAN

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FURADAN®

SOME RECOMMENDATIONS FOR STUDYING THE ENVIRONMENTAL PERSISTENCE AND FATE OF FURADAN® USED IN CONE AND SEED INSECT CONTROL PROGRAMS

by

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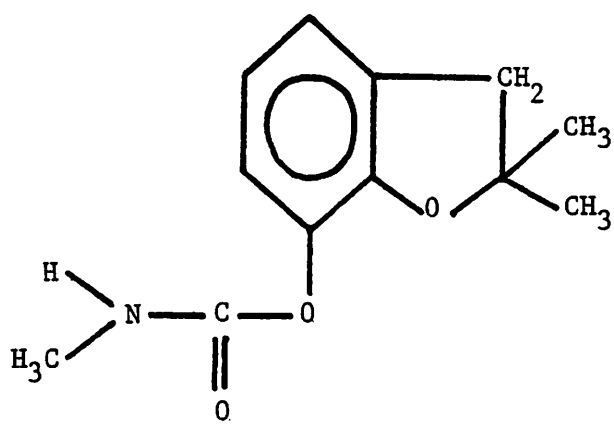
Introduction

Furadan® (common name : carbofuran) is a carbamate insecticide introduced by FMC Corporation in 1967. It is a colourless crystalline solid (m.p. 150-152°C) with a solubility of 700 ppm in water at 25°. It is highly soluble in polar solvents.



It is a systemic insecticide applied to foliage or soil (ref. Table 1 for details). The toxicological data given in literature suggest that the material is toxic to mammals (LD_{50} rats 8-14 mg/kg) and aquatic organisms (LC_{50} trout 0.28 mg/ℓ).

Use Pattern of Furadan®

Furadan® (carbafuran ; 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate) is used extensively in Canada as a broad-spectrum contact insecticide for the control of soil-borne and foliar pests. The insecticide is used in corn, strawberry, carrot, onion and turnip fields as soil or furrow treatment. Potatoes, tomatoes and other vegetables received foliar treatments. A summary of the use pattern of the chemical as given in NRCC Report No. 16740 on carbofuran is enclosed (Table 1).

No extensive use of this chemical in forestry is reported although it was used on a small scale, without success, in 1968 in Newfoundland against balsam woolly aphid.

Persistence of Furadan®

(i) Foliage

The primary degradation product which persists as glycosides in most plants is 3-hydroxycarbofuran. It could persist for a long time in conifer needles, along with the parent material as solutes dissolved in polar terpenoides and cuticular waxes present in the conifers. The concentrations present may differ as per the dosage, formulation and other post-treatment environmental factors existed in the treated area. Mungho pines, treated with the granular insecticide at 2.0g A.I./tree via soil incorporation, found to contain the active material in toxic levels (housefly) for nearly 2 years. The concentration in needles, where the transpiration was high, were 100 times greater than the buds. Similar rapid uptake, translocation and persistence are also noted in other plants. We could extrapolate that the same trend could be expected in spruce, pine (southern) and fir also.

(ii) Soils

Extensive research have shown that the persistence of carbofuran in soils depends upon, in addition to dosage, formulation (granular form stays longer), photolysis, temp., moisture content etc.:

(a) pH - lower the pH longer the persistence. Since most of the forest soils are acidic, we may expect that the material will stay longer in forest soils.

(b) Soil clay & organic matter - high clay and organic matter content increase the persistence. Soil type plays an important part in persistence.

(c) Microorganisms - carbofuran degradation is little; intensive study correlating with pH is necessary. Most likely the role of these organisms in reducing the carbofuran content in forestry soils may not be significant.

The metabolites found in soil are the 3-ketocarbofuran, carbofuran phenol and 3-ketocarbofuran phenol. The 3-hydroxycarbofuran present as a foliar residue is seldom found in soils.

(iii) Water

Carbofuran is more persistent in acidic waters and at low temperature. Since natural waters in forest areas are usually acidic, we could expect that carbofuran could persist for appreciable time in the aquatic systems ($T_{1/2}$ - pH 3 ca 20,000 h, pH 9.5 ca 66.9 min). Hydrolysis, adsorption, photolysis, volatilization and microbial action are some of the pathways for the loss of the chemical from the aquatic systems. In any treatment (broadcast, band, in-furrow and foliar) runoff is expected to contribute (significantly higher in surface and foliar applications) to the contamination of waters adjacent to the application site especially following a heavy rainfall. Periodical monitoring of nearby stream and pond waters and possibly their sediment and fish samples for carbofuran moieties is not only essential but also prudent to assess the overall impact of the chemical especially when the applied dosage is high.

Frequency of Sampling Substrates for Analysis

(i) Minimum essential monitoring work to determine the persistence of Furadan after in-furrow liquid application. (Assumption: Sept. 1st as application date and last sampling is on April 30 i.e. 270 day sampling)

(a) Foliage	control, 3, 10, 20, 60, 90, 120, 180, 240 and 270 days	- 10 samples
(b) Buds	control, 180, 240 and 270 days	- 4 samples
(c) Soil	control, 0, 10, 20, 60, 90, 120, 180, 240 and 270 days	- 10 samples
(d) Ground vegetation	control, 10, 20, 60, 180 and 240 days	- 6 samples
(e) Water (Runoff)	control, 3, 10, 20, 60, 90, 240 and 270 days	- 8 samples

[if conditions are favourable and samples available, pond and stream waters should be analysed separately as per the schedule]

Notes: (1) Should dead mammals and birds be found in the application plot or nearby areas, they should be analysed for Furadan® content in them.

(2) Each substrate in (a) to (e) should be analysed in duplicate. The S.D. should be ca 10%.

(3) In case of excessive rainfall either in the fall soon after the application or in the spring, then the frequency of sampling water in (e) should be increased. Concentration of the chemical in the runoff should be highest ca one day after the rain.

(4) If an unexpected thaw occurs after the ground freezes, sampling of water and soil should be done in as many areas as possible to check the movement of Furadan®.
(5) For checking the Furadan® treated plots by W. Fogal in 1980, foliage and soil samples should be collected and analysed. The foliage should be inspected for insects soon after sampling and processed as discussed below.

(ii) <u>Cost and Time involved in the monitoring work</u> (very conservative estimate)

Total number of samples to be analysed in (a) to (e) = 10 + 4 + 10 + 6 + 8
= 38
If done in duplication = 76 samples

At 3 samples/day/person (assuming peak of efficiency)
time involved = 78/3 = 25 man-days or 5 weeks

Approximate cost (without overhead expenses)/sample $30
Total cost $76 x 30 = $2280

<u>Notes</u>: (1) If cost and man-days are of no consideration, then the frequency of sampling could be increased to give a meaningful picture on the fate and persistence of Furadan® in different forestry substrates.
(2) Furadan® being a systemic insecticide, the material will be very likely translocated in cones and seeds of conifers (pines). This should be investigated thoroughly to study the effect of the chemical on seed germination.

<u>Sampling of Substrates for Analysis</u>

<u>Foliage</u>: Sample randomly one 20 cm midcorwn branch each from 25 selected trees in the plot. Clip the foliage using a clipper, pool and mix, put in plastic bags, label and store in a cooler packed with dry ice. Transport immediately to the analytical laboratory and store at -20°C until analysis.

<u>Buds</u>: Collect about 50g of buds and new shoots from the mid-crown of the 25 trees as above, store and transport as in foliage.

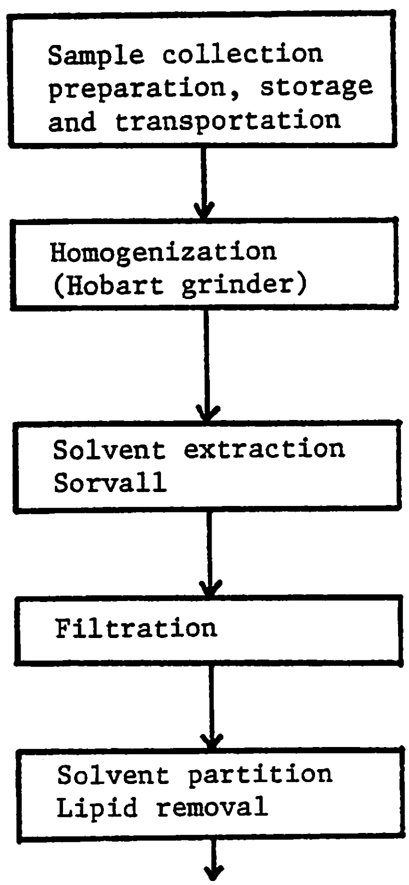
<u>Soil</u>: Collect randomly from 5 different areas in the plot by taking a strip of soil 2 cm wide, 30 cm long and 5 cm deep perpendicular to the application furrows. Remove the stones and debris using a sieve, store and transport as in foliage.

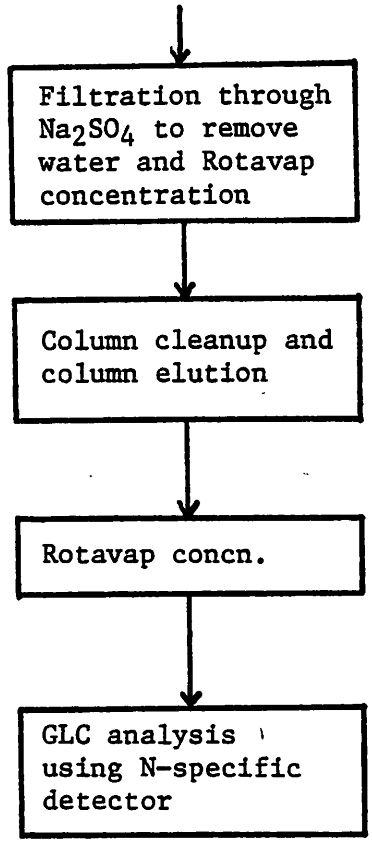
Vegetation: As under foliage (select a single indicator species).

Water: Using a beaker, collect from 10 different places top 1 cm of water (ca 100 ml) layer up to a total capacity of 1 liter. Pool them in a 2 ℓ bottle. Either extract the water in the field using dichloromethane as solvent and transport the extract in a cooler or transport the sampled water itself in a cooler packed with ice cubes to the laboratory for further extraction and analysis. Care and uniformity in sampling are necessary for the generation of meaningful data.

Analysis of Furadan®

Excellent GLC methods are available for quantifying the Furadan® residues present in various substrates. Especially by using the N-specific detector, highly sensitive and reliable residue data could be generated. Table 2 lists some of the published methods on the material. Also refer to pp 20-22 of the NRC report #16740 on this (Table 3). A flowchart containing different steps for the analysis of carbofuran in foliage is given below.





Conclusions

A brief outline on how to study the environmental fate of Furadan® used in cone and seed control program is given above. If the environmental chemistry aspect of the program is properly planned and executed, the data generated will be extremely useful not only for the registration of the chemical but also for comparing the usefulness of other insecticides with Furadan®. It is hoped that the outline presented here is useful and if any further help is needed, it will be our pleasure to help others involved in this investigation.

Table 1. Use Pattern of Furadan®

Crop	Pest	Formulation[a]	Marketing type[b]	Dosage	Directions for use
Strawberry	Meadow spittlebug, strawberry root weevil	SU	RES	538-1076 g a.i. in 1123 l/ha	BRITISH COLUMBIA: Apply only if fresh leaf notches caused by adult weevils are seen in April. Spray before the end of the first week of May (before blossoming) and repeat immediately after harvest if more fresh notches appear. Make further post-harvest applications only if fresh notches are seen before July and October. The spring treatment also controls spittlebug. Do not apply blossoming and harvest. Limitation (7)
	Strawberry weevil (blossom clipper)	SU	RES	538 g a.i./ha	EASTERN CANADA: Make one application just before the first blossoms open. Use sufficient water for good coverage. Do not apply later than first bloom. Limitation (7)
Carrot	Carrot rust fly (first generation), carrot weevil, six-spotted leafhopper	GR	COM	2241 g a.i. (from 10% granules)/ha	FURROW TREATMENT: Apply in seed furrow slightly (1.3 cm) below the seed at the time of planting. During late July and August, further sprays with another insecticide will be necessary to control late infestations (except the sixspotted leafhopper in the Atlantic Provinces). Limitation (8)
Onion (dry, from seed)	Onion maggot	GR	COM	69 g a.i. (from 10% granules)/1000 m of row	Apply with the seed in the furrow at planting time. Use only with onion seed treated with a registered fungicide for smut control. Do not use in pickling or greenbunching onions grown from sets. Limitation (8)
Pepper (green)	European corn borer	SU	RES	538 g a.i. in 1123-1404 l/ha	ONTARIO: Apply when the second generation has hatched, usually in early August. Repeat at intervals of 7 days. Limitations (1) (7)
Corn (field, sweet)	Northern corn rootworm	GR	COM	84- 112 g a.i. (from 10% granules)/1000 m of row	Apply as an 18-cm band immediately after planting. Place the band of granules over closed seed furrow and press into loose soil by means of a roller or press wheel. Harvested crop may be fed to livestock. Limitation (8)

(cont'd)

Table 1. Use Pattern of Furadan® (cont'd)

Crop	Pest	Formulation	Marketing type	Dosage	Directions for use
	European corn borer	SU	RES	538 g a.i./ha	Apply with sufficient water for good coverage. Spray not later than when first feeding is seen on foliage. For number and timing of applications, follow customary spray schedule for European corn borer control in your region. Do not apply more than 4 times per season. For second brood borers in late planting, apply before tassels show. Corn, husks and stalks may be fed to livestock. Limitations (1) (4) (7)
	Grasshoppers	SU	RES	140 g a.i./ha	Apply in sufficient water for good coverage. Do not apply more than twice per season. Limitations (1) (4)
Potato	Aphids, Colorado potato beetle, potato flea beetle, potato leaf-hopper, tarnished plant bug	SU	RES	538-807 g a.i. in 898-1123 l/ha	Apply when insects are first noticed, and repeat as necessary. Spray at a minimum pressure of 8788 g/cm². Use the high rate for heavy infestations. If Colorado potato beetle is the only insect to be controlled, reduce rate to 266 g a.i. Limitations (1) (7)
	Colorado potato beetle, potato flea beetle, leafhopper	GR	COM	298 g a.i. (from 10 granules)/ 1000 m of row	BAND TREATMENT: Apply at the time of planting in a 10-cm band in the seed furrow or drill into the soil 10 cm on each side of the row and 5 cm below the seed. Inspect crop regularly for insects, beginning in late July and spray with the flowable formulation if necessary. Limitation (8)
	Wireworms	GR	COM	298 g a.i. (from 10 granules)/ 1000 m of row	BAND TREATMENT, EASTERN CANADA AND BRITISH COLUMBIA: Apply at the time of planting in a 10-cm band in the seed furrow or drill into soil 10 cm on each side of the row and 5 cm below the seed. Limitation (8)
		GR	COM	5600 g a.i. (from 10 granules)/ ha	BROADCAST TREATMENT, ATLANTIC PROVINCES: Use broadcast treatment only when infestation is severe. Apply before planting and disc to a depth of 12.7-15.2 cm. Limitation (8)

(cont'd)

Table 1. Use Pattern of Furadan® (cont'd)

Crop	Pest	Formulation[1]	Marketing type[2]	Dosage	Directions for use
Rutabaga, turnip	Flea beetles, root maggots	SU	RES	177 g a.i./1000 m of row	Apply after seeding but before emergence. Apply as a coarse spray in a 10-cm band over the row. In Eastern Canada, make one additional application 5 weeks after seeding and another 5 weeks later (mid-August). In the Prairie Provinces, also make one additional application in early July, and another in early August. In British Columbia, make additional applications 30,50 and 70 days after seeding. Limitations (1) (2) (7)
	Root maggots	GR	COM	223-269 g a.i. (from 10 granules)/ 1000 m of row (Atlantic Provinces)	In the Atlantic Provinces, use a sub-surface applicator to apply a 10-cm band 2.5 cm below the soil surface. Close the furrow and plant the seed 1.3 cm above the centre of the band. If the machine has a fertilizer attachment, be sure that fertilizer is banded about 5 cm below the insecticide.
		GR	COM	186 g a.i. (from 10 granules)/ 1000 m of row (other provinces)	In the other provinces, apply a 10-cm band on the soil surface in front of the planter shoe and incorporate into the soil while seeding. Opening and closing the furrow gives the incorporation. Make additional applications as a spray, using the flowable formulation. Limitations (2) (8)
Surgarbeet	Sugarbeet root maggot	GR	COM	840 g a.i. (from 10 granules)/ha	Apply directly into the seed furrow at the same depth as the seed or slightly above the seed. Do not apply starter fertilizer in the same furrow. Tops and pulp from treated sugarbeets may be fed to livestock. Limitation (8)
Alfalfa	Alfalfa weevil	SU	RES	269 g a.i./ha	AIRCRAFT OR GROUND APPLICATION: Apply when 25 of the alfalfa tips show feeding damage. If the period before harvest is less than 7 days, spray stubble after harvest. Make only 1 application per crop. For ground application, use not less than 112 l/ha; if applied by air, use not less than 56 l. Limitations (1) (3) (4) (7)

(cont'd)

Table 1. Use Pattern of Furadan® (concl.)

Crop	Pest	Formulation[a]	Marketing type[b]	Dosage	Directions for use
Alfalfa, barley, flax, headlands, mustard, oats, pastures, rape, roadsides, sweet clover, wheat	Grasshoppers	SU	RES	140 g a.i./ha	AIRCRAFT OR GROUND APPLICATION: Apply in sufficient water for good coverage. Repeat as necessary, but prevent grazing. Remove cattle before spraying. May be applied by aircraft if there is no hazard of drift to inhabited areas or to other crops. Limitations (1) (3) (4) (5) (6) (7)
Mustard, rape	Flea beetles	GR	COM	224-280 g a.i./ha (5% slow-release formulation)	Mix seed and granules thoroughly in drill box and apply using a regular grain or a forage seeder. Use the higher rate for heavy infestations. Limitation (8)
		SU	RES	140 g a.i./ha	Apply about 2 weeks after seeding or when insects are first noticed. Limitations (1) (4) (5) (7)
	Red turnip beetle	SU	RES	70 g a.i./ha	Apply when insects are first noticed. Limitations (1) (4) (5) (7)
Sunflower	Grasshoppers, sunflower beetle	SU	RES	140 g a.i./ha	Apply when insects are first noticed. Do not spray after plants are more than 60 cm in height or after heads have started to form. For sunflower beetle, application by aircraft is not effective. Limitations (1) (5) (7)

[a] Formulations: GR - granular
SU - suspension

[b] Marketing types: COM - commercial
RES - restricted

TABLE 2

ANALYTICAL METHODS FOR FURADAN®

LITERATURE SURVEY

CBF

Determination of Carbofuran and 3-Hydroxy-carbofuran in small Fruits

I.H. Williams and M.J. Brown

J. Agric. Food Chem. 21:399-401 (1973)

CBF

Determination of Residues of Methyl- and Dimethylcarbamate Insecticides by Gas Chromatography of their 2,4-Dinitroaniline Derivatives

E.R. Holden, W.M. Jones, and M. Beroza

J. Agr. Food Chem. 17:56-59 (1969)

CBF

Acid Ammonium Acetate Extraction and Electron Capture Gas Chromatographic Determination of Carbofuran in Soils

J.H. Caro, D.E. Glotfelty, H.P. Freeman, and A.W. Taylor

J.A.O.A.C. 56:1319-1323 (1973)

CBF

Evaluation of Extraction Procedures for the Removal of Carbofuran and Its Toxic Metabolites from Cabbage Leaves

C.H. Van Middelem and A.J. Peplaw

J. Agr. Food Chem. 21:100-103 (1973)

CBF

Determination of Carbofuran and its Toxic Metabolites in Animal Tissues by Gas Chromatography of Their N-Trifluoroacetyl Derivatives

L. Wong and F.M. Fisher

J. Agr. Food Chem. 23:315-318 (1975)

CBF

Method for gas-chromatographic determination of ®Curateer residues in plants and soil samples, with consideration to metabolites

E. Mollhoff

Pflanz. Nach. Bayer 28:370-381 (1975)

CBF

Analysis of Carbamate Insecticides by Fluorigenic Labelling and High-Speed Liquid Chromatography

J. Chromat. Science 12:40-44 (1974)

CBF

Metabolism of Carbofuran in Mugho Pine

D.J. Pree and J.L. Saunders

J. Agr. Food Chem. 22:620-625 (1974)

CBF

Fate of Carbofuran and Its Metabolites on Strawberries in the Environment

T.E. Archer, J.D. Stokes, and R.S. Bringhurst
J. Agr. Food Chem. 25:536-541 (1977)

CBF

A Simple Spectrophotometric Method for the Determination of Carbofuran Residues

J.R. Rangaswamy, Y.N. Vijayashankar, and S.R. Prakash
J.A.O.A.C. 59:1276-1278 (1976)

CBF

Routine Methods for Analysis of Organophosphorus and Carbamate Insecticides in Soil and Ryegrass

P.T. Holland
Pestic. Sci. 8:354-358 (1977)

CBF

Effects of Light on the Fate of Carbofuran During the Drying of Alfalfa

T.E. Archer
J. Agr. Food Chem. 24:1057-1062 (1976)

CBF

Determination of the Phenolic Metabolites of Carbofuran in Plant and Animal Matrices by Gas Chromatography of Their 2,4-Dinitrophenyl Ether Derivatives

R.F. Cook, J.E. Jackson, J.M. Shuttleworth, O.H. Fullmer, and G.H. Fujie

J. Agr. Food Chem. 25:1013-1017 (1977)

CBF

Loss of Carbofuran from Rice Paddy Water: Chemical and Physical Factors

J.N. Seiber

J. Environ. Sci. Health B13(2) 131-148 (1978)

CBF

Formation of the N-Trifluoroacetate of Carbofuran

R.J. Ross

J. Agr. Food Chem. 25:1209-1210 (1977)

CBF

Direct Analysis of Carbofuran and Two Nonconjugate Metabolites in Crops by High-Pressure Liquid Chromatography with UV Absorption Detection

J.F. Lawrence and R. Leduc

J. Agr. Food Chem. 25:1362-1365 (1977)

CBF

A High-Pressure Liquid Chromatographic Method for the Determination of Carbofuran Residues in Soil and Water

T.R. Nelsen and R.F. Cook

J. Agr. Food Chem. 27:1186-1190 (1979)

CBF

The Degradation of Carbofuran in Paddy Water and Flooded Soil of Untreated and Retreated Rice Fields

R. Siddaramappa, A.C. Tirol, J.N. Seiber, E.A. Heinrichs and I. Watanabe

J. Environ. Sci. Health B13:369-380 (1978)

CBF

Derivatization of Several Carbamate Pesticides with Methanesulfonyl Chloride and Detection by Gas-Liquid Chromatography with the Flame Photometric Detector: Application to Residues of Carbaryl on Lentil Straw

Jay C. Maitlen and Leslie M. McDonough

J. Agric. Food Chem. 28:78-82 (1980)

CBF

Ultrasonic Extraction of Carbofuran Residues from Radishes

W.B. Wheeler, N.P. Thompson, R.L. Edelstein, and R.T. Krause

Bull. Environm. Contam. Toxicol. 21:238-242 (1979)

CBF

Persistence and Uptake of Carbofuran in a Humic Mesisol and the Effects of Drying and Storing Soil Samples on Residue Levels

R. Greenhalgh and A. Belanger

J. Agric. Food Chem. 29:231-235 (1981)

CBF

Determination of Carbofuran and 3-Hydroxycarbofuran Residues in Plant Tissue by Nitrogen Selective Gas Chromatography

Thomas R. Nelsen and Ronald F. Cook

J. Agric. Food Chem. 28:98-102 (1980)

CBF

Direct Analysis of Carbofuran and 3-Hydroxycarbofuran in Rape Plants by Reverse-Phase High-Pressure Liquid Chromatography

Young W. Lee and Neil D. Westcott

J. Agric. Food Chem. 1980. 28, 719-722

Table 3. Techniques for determining carbofuran in various substrates

Substrate	Extraction, solvent, cleanup	Derivative	Quantitation	% Recoveries	Metabolites	Sensitivity (mg/kg)	Reference
corn	aq. acid/acetonitrile-hexane/Nuchar-Attaclay-silica gel	-	GC/MCD [N]	70	C, OH-C	0.05 - 0.1	Cook 1968 Cook et al. 1969
soil	aq. acid	-	GC/MCD [N]	70	C, OH-C	0.5 - 10.0	Cook 1968
spinach	dichloromethane/KOH	2,4-DNP	GC/ECD 2% XE-60	105	C	0.05	Holden et al. 1969
tomato, foliage	aq. acid/blend alumina/florisil	trichloroacetate	GC/ECD 7% DC-200	67 - 139	C, OH-C, KC	0.04 0.01 0.04	Butler and McDonough 1971
lettuce	aq. acid/Nuchar-Attaclay-30% hexane-ethyl acetate	-	GC/AFID Porapak P	100	C, OH-C	0.05	Van Middelem et al. 1971
soil, corn, water	aq. ammonium acetate/shake	2,4-DNP	GC/ECD 3% OV-17	61 - 92	C	0.1	Caro et al. 1973b
alfalfa, apples, beans, corn, eggs, lettuce, milk, peanuts, etc.	aq. acid/Nuchar-Attaclay silica gel	-	GC/MCD [N] 20% SE 30	-	C, OH-C, KC	0.1 - 0.5	Cook 1973
strawberries, raspberries, blueberries, cranberries	aq. acid/reflux alumina/silica gel	-	GC/E Cond D [N] 6% OV210 4% OV-101	86	C, OH-C	0.2	Williams and Brown 1973
corn, beans, cabbage, turnips	CH₃CN/blend	2,4-DNP	GC/ECD 100% DC-200	90 - 110 87 - 100	C, OH-C, KC	0.05	Holden 1973, 1975
corn	-	2,4-DNP	GC/ECD 3% DC-200	93 - 100	C, OH-C, KC	0.01 (OH-C) 0.2 (C, KC) 0.2, 0.01, 0.2	Turner and Caro 1973

(cont'd)

Table 3. Techniques for determining carbofuran in various substrates (cont'd)

Substrate	Extraction, solvent, cleanup	Derivative[a]	Quantitation[b]	% Recoveries	Metabolites[c]	Sensitivity (mg/kg)	Reference
soil, alfalfa	aq. acid/alumina/ methanol/gel	-	TLC/Col.	-	C, OH-C, KC CP, OH-CP, KCP	-	Getz 1974
animal tissue, shrimp, blackbird, mullet	aq. acid/florisil	TFA	GC/ECD 3% DC-200	84: C, OH-C 73: KC	C, OH-C, KC	0.5(C) 0.05(OH-C) 0.07(KC)	Wong and Fisher 1975
lettuce, cabbage, soil	acetone/tumbling	sulfonic esters	GC/ECD 5% UCW-98	-	C	0.05	Moye 1975
soil	aq. acid/methanol blend	on-column/ trans ester- ification	GC/AFID	-	C, OH-C OH-C glycoside	0.1	Möllhoff 1975
potatoes, sugar beets, grain, straw, tomatoes, onions, carrots, cauliflower, maize, lettuce, cabbage	methanol blend	on-column/ trans ester- ification	GC/AFID	-	C, OH-C OH-C glycoside	0.1	Möllhoff 1975
carrots	aq. acid/alumina	-	GC/E Cond D [N]	-	C, OH-C	-	Finlayson *et al.* 1976
corn, peanuts, peppers, potatoes, soybeans, tobacco	aq. acid/reflux/ alumina/carbon/ Na_2SO_4	2,4-DNP	GC/E Cond D [N] 3%-Apiezon, 8% OV-3	66 - 93 C 63 - 105 OH-C	C, OH-C, KC CP, OH-CP, KCP	0.1 (except tobacco 0.5)	Fullmer 1976
alfalfa	aq. acid/florisil	TFA/PFB	GC/ECD 5% SE-30, 5% Dow 710	-	C, OH-C, KC CP, OH-CP, KCP	0.1	Archer 1976
soil	methanol/CH_2Cl_2/ shake 2:5 alumina	-	GC/E Cond D [N]	-	C, OH-C	-	Williams *et al.* 1976
soil	chloroform-diethyl ether/methanol	-	TLC/Colori- metric	57 - 74	C	-	Venkateswarlu *et al.* 1977

(cont'd)

Table 3. Techniques for determining carbofuran in various substrates (concl.)

Substrate	Extraction, solvent, cleanup	Derivative[a]	Quantitation[b]	% Recoveries	Metabolites[c]	Sensitivity (mg/kg)	Reference
strawberries	aq. acid/blend/ silica gel	TFA/PFB	GC/EC 5% SE-30	77 - 100	C, OH-C, KC CP, OH-CP, KCP	0.05 (C) 0.01 (OH-C) 0.01 (KC)	Archer et al. 1977
potatoes, milk, cow tissue, eggs, poultry tissue	aq. acid/reflux or acetone/florisil/ carbon	2,4-DNP	GC/MCD	69	CP, OH-CP, KCP	0.05 - 0.1	Cook et al. 1977
carrots, turnips, potatoes, corn, cabbage	acetone/blend florisil	-	HPLC/UV Li Chromosorb Si 60	68 - 110	C, OH-C, KC	0.05 (C) 0.05 (OH-C) 0.02 (KC)	Lawrence and Leduc 1977
carrots, celery, tomatoes, corn	aq. acid/reflux/ no cleanup	HFB	GC/MS [single ion monitoring]	-	C, OH-C, KC CP, OH-CP, KCP	0.02	Chapman and Robinson 1977
corn, potatoes, turnip, wheat	acetone/blend florisil	-	GC/E Cond D [Cl]	85 - 100	C, OH, C, KC	-	Lawrence et al. 1977
corn	aq. acid/reflux/ Nuchar-Attaclay- silica gel	-	GC/E Cond D [N] 10% OV-3	-	C, OH-C	0.4 (C) 0.3 (OH-C)	Shuttleworth 1977
soil	chloroform tumble	HFB	GC/E Cond D 5% XE-60	80	C, KC	0.02	Miles and Harris 1978
soil	aq. acid/reflux	-	GC/AFID	85 - 100	C, OH-C, KC	0.02 (C) 0.02 (OH-C) 0.01 (KC)	Greenhalgh 1978

[a] 2,4-DNP = 2,4-dinitrophenyl, TFA = trifluoroacetyl, PFB = pentafluorobenzyl, HFB = heptafluorobutyl.

[b] E Cond D = electrolytic conductivity detector, [N] = nitrogen, TLC = thin layer chromatography, AFID = alkali-flame ionization detector, MCD = microcoulometric detector, GC = gas chromatography, HPLC = high pressure liquid chromatography.

[c] C = carbofuran, OH-C = 3-hydroxycarbofuran, KC = 3-ketocarbofuran, CP = carbofuranphenol, OH-CP = 3-hydroxycarbofuran phenol, KCP = 3-ketocarbofuran phenol.