Determination of Carbofuran and Its Carbamate Metabolite Residues in Corn Using a Nitrogen-Specific Gas Chromatographic Detector

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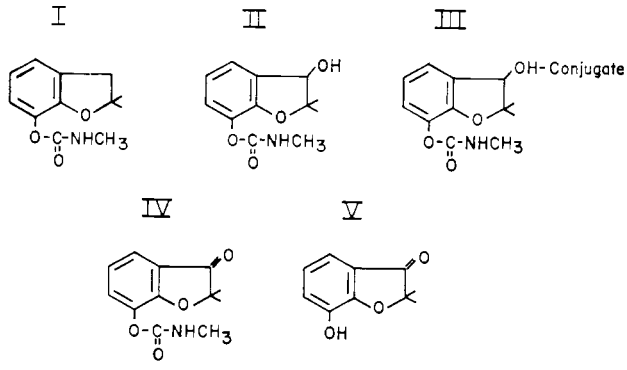
A gas chromatographic method capable of determining carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) and 3-hydroxycarbofuran (2,3-dihydro-3-hydroxy-2,2-dimethyl-7-benzofuranyl methylcarbamate) residues in field corn is presented. The intact methylcarbamate residues were determined using a nitrogen-specific microcoulometric detection system. An acid hydrolysis converted the water-soluble conjugated residue forms to the organoextractable aglycone forms. Corn stover and corn cob samples required a silica gel–Nuchar-Attaclay column cleanup. Corn kernel samples required both an acetonitrile-hexane partition to remove oil and a silica gel–Nuchar-Attaclay column cleanup. Average recoveries were 70% for carbofuran and 3-hydroxycarbofuran for the various corn samples at fortification levels from 0.05 to 0.9 p.p.m.

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) is a broad-spectrum insecticide-nematocide which has demonstrated excellent biological efficacy on a wide variety of crops (Cox, 1966; Pass, 1966; Turnipseed, 1967). It is effective as both a contact toxicant and a systemic toxicant (Dominick, 1967; Hofmaster *et al.*, 1967; Shorey and Hale, 1967).

Specifically, soil-incorporated applications of carbofuran have provided effective control of the corn rootworm (Sechriest, 1967). Because of its systemic nature, any carbofuran taken from the soil by the root system of the corn plant could result in the distribution of residues throughout the entire corn plant. Therefore, an analytical method capable of determining carbofuran and/or carbofuran metabolites in field corn was required.

The metabolism of carbofuran in corn was investigated by Stanovick (1967, 1968) using ring C^{14}-labeled and carbonyl C^{14}-labeled carbofuran. Similar investigations were conducted in other plant systems by Knaak *et al.* (1968) and Metcalf *et al.* (1968). The mechanism of the metabolic pathway involved oxidation followed by conjugation at the three position of the benzofuran ring and/or hydrolysis followed by conjugation at the seven position of the benzofuran ring. Carbofuran (I), 3-hydroxycarbofuran (II), and 3-hydroxycarbofuran glycoside (III) were the only carbamate residues found in corn by the metabolic study. No accumulation of 3-ketocarbofuran (IV) in the corn plant by the oxidation of 3-hydroxycarbofuran was evident. Metcalf *et al.* (1968) indicated the 3-ketocarbofuran to be hydrolytically unstable and rapidly converted to 2,3-dihydro-7-hydroxy-2,2-dimethyl-3-oxobenzofuran (V), which in turn could be conjugated.

The radio tracer work of Stanovick (1967) also demonstrated that the conjugated forms of the carbamate



residues could be completely released to the aglycone forms, as shown in Figure 1, using a hot acid digestion. Table I data illustrate the quantitative nature of the reaction.

Solvent extractions of the corn plant were not capable of removing the conjugated residues.

Based on the above conclusions, neither the thiophosphorylation method of Bowman and Beroza (1967) nor the trichloroacetylation method of Butler and McDonough (1968) was directly applicable to the analysis of conjugated carbofuran metabolite residues because solvent extraction techniques were used. In addition, acid-hydrolyzing the crop to release the conjugated residues yielded a variety of phenolic plant materials which could then derivatize and interfere with the methods.

Therefore, a highly sensitive residue method capable of directly determining free and conjugated carbofuran carbamate metabolites was developed using gas chromatography and the nitrogen-specific microcoulometric detection system of Martin (1966).

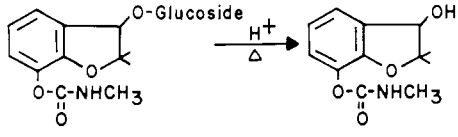


Figure 1. Conversion of conjugated to aglycone form

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Table I. Recovery of Radioactivity from Corn Grown in Soil Treated with Ring C^{14}-Labeled Carbofuran

Sample Description	Extraction Method	P.P.M. Carbofuran Equivalents
Corn stover, 104-day	Benzene	2.3
	Methanol	13.4
	Residue	4.7
	Total	20.4
Corn stover, 104-day	Methylene chloride extraction of acid-hydrolyzed crop	18.9

$$\text{Recovery} \rightarrow \left(\frac{\text{methylene chloride}}{\text{exhaustive extraction total}} \times 100\right) = 93\%$$

APPARATUS

Round-bottomed flask, 1000-ml. with 50/50 ⅎ neck opening and a 50/50 to 24/40 ⅎ neck-reducing adapter.

Liebig condenser, 200-mm. jacket and 24/40 ⅎ inner drip joint bottom.

Separatory funnel, 2000-ml. and 250-ml.

Liquid chromatographic column, 20-mm. I.D. × 400 mm. with porous fritted disk.

Gas chromatograph, Micro-Tek Model MT-220 (or equivalent) equipped with a Dohrmann microcoulometric nitrogen detection system (Model S-200 pyrolysis furnace, Model C-200-A microcoulometer, and Model T-400-H nitrogen detector) and a 1.0-mv. recorder with a disk chart integrator.

REAGENTS

Sodium lauryl sulfate, U.S.P. (Fisher).

Methylene chloride, laboratory-distilled or equivalent.

Acetonitrile, laboratory-distilled.

Nuchar-Attaclay (Kensington Scientific Co.).

Silica gel, Grade 923, Davison Chemical Code 923–08–08–226 (distributed by Fisher Chemical Co.).

Hydrogen, compressed gas, ultra-high purity grade or equivalent.

Nickel turnings (2-foot × 3-inch pure nickel bar, Whitehead Metals, lathe turned).

Analytical standards, Niagara Chemical Division, FMC Corp., Middleport, N. Y. 14105.

PROCEDURE

Corn Kernels. SAMPLE PREPARATION. Chop and blend each batch of corn kernels using a Hobart food cutter to provide a homogeneous sample. Package the chopped kernel samples in polyethylene bags and store at 0° C. until needed for analysis.

EXTRACTION. Place 70 grams of chopped corn kernels in a 1000-ml. round-bottomed flask containing a magnetic stirring bar. Add 600 ml. of 0.25*N* hydrochloric acid. Connect the round-bottomed flask to a Liebig condenser using a 50/50 to 24/40 ⅎ neck adapter. Reflux the crop-acid mixture for 1 hour using a heating mantle. Swirl the flask contents by hand during the initial heating period and then continuously stir the mixture with a magnetic stirring bar. Fortify check kernel samples prior to the addition of acid.

After 1 hour of refluxing, remove the round-bottomed flask from the heating mantle and filter the hot sample through glass wool into a 1000-ml. Erlenmeyer flask. Wash the reflux flask and glass wool with an additional 300 ml. of hot 0.25*N* hydrochloric acid. Cool the filtrate for 1 hour at −10° C. and transfer into a 2000-ml. separatory funnel. Add ca. 250 mg. of sodium lauryl sulfate to the filtrate and mix. Extract the aqueous phase three times with 600 ml. of distilled methylene chloride. Combine the methylene chloride extracts and dry over anhydrous sodium sulfate.

Concentrate the dried extract to ca. 30 ml. using a 1000-ml. Kuderna-Danish evaporator. Add 50 ml. of acetonitrile to the concentrated extract in the evaporator and concentrate to about 10 ml.

CLEANUP. Transfer the acetonitrile concentrate to a 250-ml. separatory funnel. Rinse the evaporator into the separatory funnel with additional acetonitrile to a final volume of about 25 ml. Extract the acetonitrile twice with 15 ml. of hexane saturated with acetonitrile. Discard the hexane layers. Transfer the extracted acetonitrile into a thoroughly cleaned evaporator and concentrate to 2 ml. Transfer to a 250-ml. separatory funnel, rinsing the evaporator with 100 ml. of 0.25*N* hydrochloric acid. Extract the aqueous phase three times with exactly 50 ml. of distilled methylene chloride. Combine the methylene chloride extracts and dry over anhydrous sodium sulfate. Filter the dried extract and accurately record the volume recovered for use in the final calculations. Thoroughly clean all the evaporators used in the acetonitrile-hexane partition with Chromerge and then rinse with distilled water, followed by acetone to minimize potential interferences.

Slurry 7 grams of Nuchar-Attaclay with 80 ml. of distilled methylene chloride and pour into a 20-mm. I.D. × 400-mm. liquid chromatography column containing a glass wool plug in the bottom. Allow the Nuchar-Attaclay to pack tightly in the column, using suction provided by a water aspirator through a 500-ml. filter flask. Rinse the sides of the column with distilled methylene chloride and place a thin glass wool plug on top of the packed Nuchar-Attaclay. Add 80 ml. of distilled methylene chloride to the column using suction. Rinse down the sides of the column with distilled methylene chloride. Cap the column with a plug of glass wool. Drain the solvent to the top of the glass wool cap. (The solvent level should always be maintained above the absorbent level during preparation of the column.) Discard the washings collected in the 500-ml. filter flask.

Add the dried methylene chloride filtrate (about 135 ml.) from the above acetonitrile partition to the Nuchar-Attaclay–silica gel column. Rinse the graduate into the column with an additional 15 ml. of distilled methylene chloride. Start collection of the sample immediately, using suction. When the solvent level reaches the top glass wool plug, add 100 ml. of 30%

(v./v.) hexane–ethyl acetate. Maintain continuous collection until no solvent remains on the column.

Transfer the combined methylene chloride and ethyl acetate–hexane fractions into a 500-ml. evaporator and concentrate to about 25 ml. Add 100 ml. of benzene to the same evaporator and concentrate the solution to about 2 ml.

ANALYSIS. Concentrate the 2-ml. sample to less than 1 ml. using a gentle stream of dry air. Dilute the sample to a final volume of exactly 1.0 ml. with benzene. Inject a suitable aliquot—e.g., 20 μl.—into a gas chromatograph equipped with a Dohrmann microcoulometric nitrogen detection system, operating at the following conditions:

Injection port temperature, 225° C.

Column, 2-feet by ¼-inch O.D. aluminum tubing packed with 3.5 grams of 20% (w./w.) SE-30 on 60- to 80-mesh Gas-Chrom Z and silanized as described below.

Column temperature, 165° C.

Carrier gas, hydrogen, 20 p.s.i. at inlet.

Column flow rate, 300 ml. per minute.

Transfer line temperature, 200° C.

Pyrolysis furnace: Inlet 200° C. Center 850° C. Outlet 450° C.

Reactant flow rate, 200 ml. per minute.

Auxiliary flow rate, 150 ml. per minute.

Gain setting, Hi.

Hi gain setting, 65.

Bias setting, 100 mv.

Range (attenuation), 200 ohms.

Chart speed, 0.5 inch per minute.

With the instrument equilibrated under the above conditions, a retention time—i.e., from the point of injection to the peak center—of 3.2 minutes for carbofuran and 5.4 minutes for 3-hydroxycarbofuran should be obtained.

Corn Stover and Corn Cobs. Place 50 grams of chopped corn stover or corn cobs in a 1000-ml. round-bottomed flask and proceed as for corn kernels.

Concentrate the combined initial methylene chloride extracts (about 1800 ml.) to about 150 ml. in an evaporator. Add the concentrate directly to the Nuchar-Attaclay–silica gel column and proceed as for corn kernels.

CALCULATIONS

The quantity of hydrogen ions produced in the nitrogen detector by the generator (anode-cathode) circuit above the steady-state level controlled by the bias set proceeds according to Faraday's law. Therefore, the amount of hydrogen ion produced is equivalent to the amount of ammonia introduced into the cell from the reduction oven and the amount of ammonia is proportional to the amount of nitrogen contained in the original compound. Figure 2 presents a top view schematic diagram of the nitrogen titration cell and the equations involved in its operation.

The quantity of electrical energy needed to produce an appropriate quantity of hydrogen ion is accurately monitored by the microcoulometer and subsequently displayed on a strip chart recorder as a function of time. By Ohm's law, the millivolt-seconds per ohm displayed on the recorder as a peak area are proportional to the coulombs (ampere-seconds) required for the regeneration of titrant consumed by the incoming sample. Therefore, the gas chromatographic peak areas may be directly converted to a quantitative value without the necessity of a calibration curve by using the following equation:

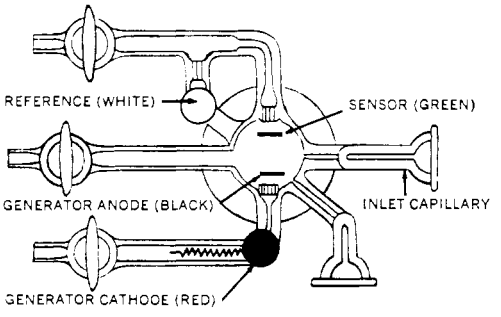

Figure 2. T-400-H titration cell

Cell reaction

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + H^+ \rightarrow NH_4^+ + H_2O$$

Generator reaction

1. $\frac{1}{2} H_2 \rightarrow H^+ + e^-$
2. $H_2O + e \rightarrow OH^- + \frac{1}{2} H_2$

$$\text{Micrograms} = \frac{\text{peak area (sq. inches)} \times C \times D}{\text{range (ohms)} \times \text{per cent nitrogen in compound}} \quad (1)$$

where C = recorder sensitivity =

$$\frac{\text{minutes}}{\text{inch}} \times \frac{\text{millivolts}}{\text{inch}}$$

and where D = conversion constant = 870.4.

For a 0.1-mv. per inch recorder operating at a speed of 0.5 inch per minute, Equation 1 reduces to:

$$\text{Micrograms} = \frac{\text{peak area (sq. inches)} \times 1741}{\text{range (ohms)} \times \text{per cent nitrogen in compound}} \quad (2)$$

A complete discussion of the above formula derivation is given in the operating instruction manual for the Dohrmann microcoulometric titrating system.

Using Equation 2, mathematically convert the appropriate peak areas associated with the treated corn kernel samples into micrograms of carbofuran (6.33% nitrogen) and/or 3-hydroxycarbofuran (5.90% nitrogen). Correct the micrograms found above for the method fortification recoveries. Compute the residue values in parts per million based on the corrected micrograms found per gram of sample size used corrected for the volume loss incurred in the extraction and filtration step following the acetonitrile-hexane partition.

Prepare a standard solution containing 10 μg. of carbofuran per milliliter of benzene. Inject appropriate aliquots—i.e., 10 to 20 μl.—of the standard solution into the microcoulometer nitrogen system to establish the instrument efficiency—i.e., ratio of micrograms detected to micrograms injected. Periodically during a

series of determinations, inject additional appropriately sized aliquots of the standard solution to ensure that the instrument efficiency has remained reasonably constant.

GAS CHROMATOGRAPHY

Glass injection port liners were used in the gas chromatograph to provide a more inert surface for the vaporization process. The glass port also functioned as a readily removable and cleanable trap for some of the higher boiling materials in the sample. A small piece of glass wool was placed in the middle of the injection port to provide a greater vaporizing surface and act as an additional trap. A clean port was installed after injecting about ten treated samples.

The methyl silicone column packing was prepared using the following technique. Fifty grams of SE-30 were dissolved in 500 ml. of ethyl acetate using continuous stirring. The SE-30 was precipitated from the solution by adding 500 ml. of ethanol and then washed twice with additional 100-ml. portions of ethanol. The purified SE-30 was gently heated to remove all traces of the ethanol. Forty grams of 13% (w./w.) purified SE-30–ethyl acetate solution was then poured into a liquid chromatographic column packed with 18 grams of rescreened 60- to 80-mesh Gas Chrom Z. The solid support was allowed to become completely wet with the liquid substrate solution by gravity. A small amount of the substrate solution passed through the tube. Light nitrogen pressure was then applied to the chromatographic column to dry the packing.

Long thermal preconditioning times for properly prepared methyl silicone columns were not necessary. However, considerable effort must be taken to provide a "nonabsorptive" packing to ensure the successful gas chromatography of methylcarbamates. "In place" silanizing of the column at 75° C. with hexamethyldisilazane and dimethyldichlorosilane (10 × 50 μl.) was useful for deactivating the column system.

Daily pretreatments of the gas chromatograph with injections of sample types to be analyzed were used to ensure equilibrium of the system prior to the quantitation of any data.

A heated ¼-inch O.D. shaped aluminum tube was used to transfer the samples eluting from the gas chromatographic column to the pyrolysis oven. The aluminum transfer line was thoroughly degreased prior to installation, using a 5% aqueous sodium hydroxide solution.

The quartz combustion tube used in the pyrolysis furnace was a constant 9-mm. i.d. over the entire length and terminated with a 18/9 ball joint. The standard quartz tube supplied with the furnace—i.e., 22-mm. O.D. center—did not appear to have satisfactory flow characteristics for the quantitation of microgram amounts of pesticides.

Solvent-degreased nickel turnings were used as the reduction catalyst. The combustion tube was packed with about 10 cm. of nickel turnings. Initial conditioning of the nickel turnings in the pyrolysis furnace under a flowing hydrogen atmosphere at 950° C. is required to remove sulfides and other impurities. After 24 hours of hydrogen conditioning, the pyrolysis furnace temperature was reduced to room temperature and the system purged with pure helium. Pure oxygen was then passed over the nickel turnings and the pyrolysis furnace temperature raised to 850° C. After 8 hours of oxygen conditioning, the pyrolysis furnace temperature was again reduced to room temperature and the system purged with pure helium. Hydrogen gas was again applied to the nickel turnings and the pyrolysis furnace temperature raised to 850° C. (Considerable care should be taken to ensure that the pyrolysis furnace is at room temperature and the system purged when alternating the conditioning gases to avoid any possibility of explosion.) A "zinc mirror" may form on the cool end of the quartz tube under the above conditions. If the mirror cannot be completely removed using nitric acid, a new quartz tube should be repacked with the conditioned nickel and used. A combustion tube packed and conditioned as described above functioned perfectly for over 1000 treated sample injections.

The 18/9 ball joint end of the combustion tube is designed to allow the attachment of a glass insert rod used as an acid scrubber. Potassium carbonate was used to pack the glass insert in this laboratory. However, barium oxide, strontium hydroxide, or any alkaline earth salt having a high melting point should be adaptable. The packed scrubber was maintained at 450° C. to allow the ammonia formed in the reduction oven to pass quantitatively, but to remove the acid gases formed.

The platinum generator electrodes of the nitrogen cell should require only occasional replating. Care should be taken that the platinum reference electrode is free from surface air bubbles. Positioning of the cell cap is important, as the noise and sensitivity levels are dependent, to a degree, on that positioning.

High frequency noise from the nitrogen cell may be encountered at the higher attenuation settings. Incorporating a 500-microfarad capacitor across the positive and negative input leads to the recorder and a 2000- to 10,000-ohm resistor in series with the positive input lead effectively reduced the cell noise. The optimum ohm value for the resistor was dependent upon the individual nitrogen cell and recorder characteristics.

RESULTS AND DISCUSSION

Figure 3 illustrates a typical gas chromatogram of a standard solution containing 0.2 μg. (12 ng. of nitrogen) of carbofuran and 0.2 μg. of 3-hydroxycarbofuran. Average instrument efficiencies of 77 and 60%, respectively, were obtained for carbofuran and 3-hydroxycarbofuran.

The method described above for corn kernels will allow the accurate quantitation of carbofuran and 3-hydroxycarbofuran down to 0.05 p.p.m. (0.061 μg. per 1.22-gram sample, injected). However, 0.025 p.p.m. (twice the noise level) can readily be detected by the method. Corn kernel check samples were fortified from 0.05 to 0.6 p.p.m. Fortification recovery values ranged from 57 to 84% for carbofuran and from 51 to 101% for 3-hydroxycarbofuran. The average recovery was

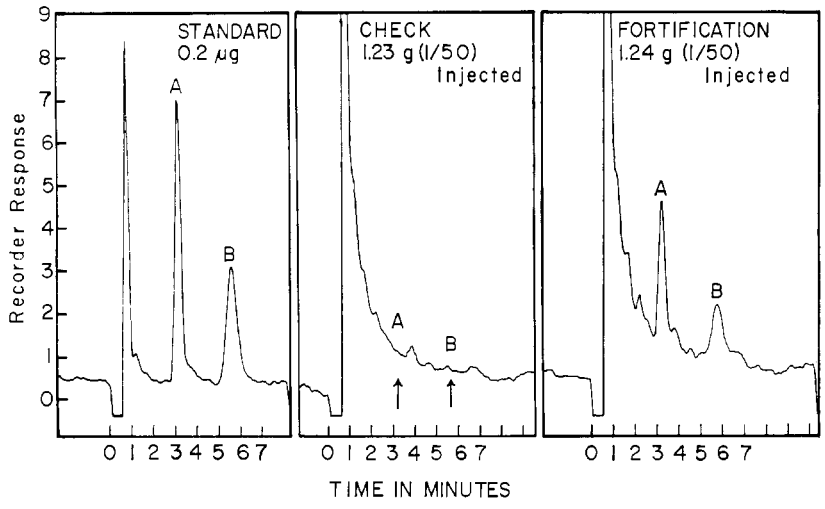

Figure 3. Typical gas chromatograms of corn kernel extracts

A. Carbofuran
B. 3-Hydroxycarbofuran

72% for carbofuran and 71% for 3-hydroxycarbofuran (Table II). Figure 3 also illustrates a typical gas chromatogram of a corn kernel check and a check fortified at 0.1 p.p.m. Occasional corn kernel check samples yielded a minor crop interference which calculated as "apparent" carbofuran. However, no interference with the method was noted from captan, diuron, Baygon. or atrazine.

The method as described for corn stover and corn cobs had a sensitivity of 0.1 p.p.m. for carbofuran and 3-hydroxycarbofuran. Corn stover and corn cob samples were fortified from 0.10 p.p.m. (0.05 μg. per 0.5-gram sample injected) to 0.9 p.p.m. Fortification recovery values ranged from 54 to 85% for carbofuran and from 51 to 86% for 3-hydroxycarbofuran, averaging 63% for carbofuran and 67% for 3-hydroxy-

Table II. Recovery of Carbofuran and 3-Hydroxy Carbofuran from Corn Kernels and Corn Stover

Carbofuran Injected		3-Hydroxycarbofuran Injected		Carbofuran Recovered		3-Hydroxycarbofuran Recovered		% Recovery	
μg.	P.p.m.	μg.	P.p.m.	μg.[a]	P.p.m.[a]	μg.[a]	P.p.m.[a]	Carbofuran	3-Hydroxycarbofuran
				CORN KERNELS					
0 061	0.05	0.061	0.05	0.0436	0.0357	0.0617	0.0506	71.4	101.0
0.062	0.05	0.062	0.05	0.0388	0.0313	0.0343	0.0277	62.6	55.4
0.128	0.1	0.128	0.1	0.0735	0.0574	0.0664	0.0519	57.4	51.9
0.124	0.1	0.124	0.1	0.0928	0.0748	0.0913	0.0736	74.8	73.6
0.124	0.1	0.124	0.1	0.0893	0.0720	0.101	0.0815	72.0	81.5
0.254	0.2	0.254	0.2	0.156	0.123	0.128	0.101	61.5	50.5
0.246	0.2	0.246	0.2	0.193	0.157	0.183	0.149	78.5	74.5
0.246	0.2	0.246	0.2	0.200	0.163	0.157	0.128	81.5	64.0
0.191	0.3	0.191	0.3	0.161	0.253	0.184	0.289	84.3	96.3
0.254	0.4	0.254	0.4	0.185	0.292	0.145	0.229	73.0	57.3
0.186	0.6	0.186	0.6	0.134	0.432	0.141	0.454	72.0	75.7
							Av.	71.7	71.0
				CORN STOVER					
0.05	0.1	0.05	0.1	0.0286	0.0571	0.0294	0.0587	57.1	58.7
0.10	0.2	0.10	0.2	0.0535	0.107	0.0860	0.172	53.5	86.0
0.10	0.2	0.10	0.2	0.0575	0.115	0.0685	0.137	57.5	68.5
0.15	0.3	0.15	0.3	0.0820	0.164	0.0835	0.167	54.7	55.7
0.15	0.3	0.15	0.3	0.100	0.200	0.0975	0.195	66.7	65.0
0.20	0.4	0.20	0.4	0.113	0.225	0.142	0.283	56.5	70.8
0.25	0.5	0.25	0.5	0.152	0.303	0.182	0.363	60.6	72.6
0.25	0.5	0.25	0.5	0.199	0.397	0.13	0.26	79.4	52.0
0.15	0.6	0.15	0.6	0.0928	0.371	0.0758	0.303	61.8	50.5
0.175	0.7	0.175	0.7	0.148	0.592	0.146	0.583	84.6	83.3
0.225	0.9	0.225	0.9	0.142	0.568	0.154	0.617	63.0	68.6
						Av. of 11 fortifications		63.2	66.5

[a] Corrected for column efficiency (corn kernels—carbofuran 77%, 3-hydroxycarbofuran 60%; corn stover—carbofuran 82%, 3-hydroxycarbofuran 60%) and check values.

carbofuran (Table II). Figure 3 also represents a typical gas chromatogram for corn stover and corn cob samples. No interference for corn stover and corn cobs was noted for parathion, diuron, linuron, carbaryl, Baygon, or atrazine.

Although not illustrated here, the corn kernel method will readily allow the quantitative detection of 3-keto-carbofuran (retention of 4.3 minutes) if present.

Having the acid digestion solution cold during the initial methylene chloride extraction and using sodium lauryl sulfate prevented the formation of emulsions.

Precautions should be taken to avoid solvent contact with the rubber filter ring seal in the column cleanup step or extraneous peaks may result in the gas chromatogram.

Radiotracer studies indicated 80 to 90% of the carbamate residues found in aged corn samples to be 3-hydroxycarbofuran or 3-hydroxycarbofuran glycoside. Therefore, if no 3-hydroxycarbofuran is evident in a given gas chromatogram, it is unlikely that any carbofuran will be present in the sample.

Radiolabeled carbofuran was used to validate the methods as to extraction efficiency as well as all subsequent steps. Over-all method recovery values obtained using gas chromatography were in excellent agreement with radiolabeled recovery values.

Presented in the initial phase of the method is a practical analytical technique for quantitatively releasing water-soluble conjugated forms of pesticide residues to the aglycone forms. Also demonstrated is the ability to gas-chromatograph intact methylcarbamates. The highly sensitive and specific microcoulometric nitrogen detection system discussed here should be readily adaptable to the determination of any nitrogen-containing material that will gas-chromatograph.

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