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Determination of Residues of Karbutilate and Its Major Metabolites in Water, Soil, and Grass by High-Pressure Liquid Chromatography

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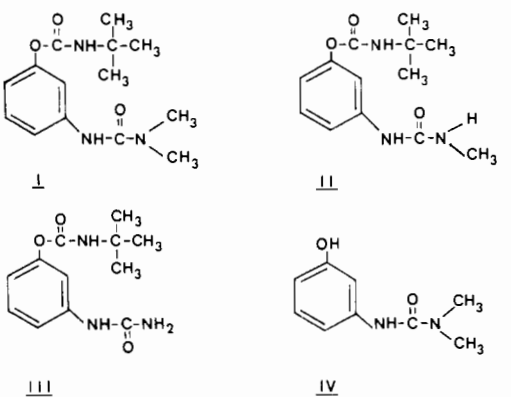
A high-pressure liquid chromatographic (HPLC) method was developed for the determination of residues of karbutilate (3-[[(dimethylamino)carbonyl]amino]phenyl (1,1-dimethylethyl)carbamate), its hydrolysis product *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and its demethylated metabolites monomethyl karbutilate (3-[[(methylamino)carbonyl)]amino]phenyl (1,1-dimethylethyl)carbamate) and demethyl karbutilate (3-[(aminocarbonyl)amino]phenyl (1,1-dimethylethyl)carbamate), in water, soil, and grass. Recoveries of karbutilate and its degradation products from water ranged from 89 to 103%. The lower limit of sensitivity of the method is 0.01 ppm for karbutilate and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and 0.02 ppm for monomethyl karbutilate. The recovery of karbutilate and its carbamate metabolites from soil ranged from 84 to 95%. For residues in grass, the carbamates are converted to the corresponding phenols, which are analyzed by HPLC. The recovery of karbutilate and its carbamate metabolites from grass ranged from 80 to 87%. The lower limit of sensitivity of the method for residues in soil and grass is 0.1 ppm for karbutilate and 0.2 ppm for monomethyl karbutilate and demethyl karbutilate.

Karbutilate (I) (3-[[(dimethylamino)carbonyl]amino]-phenyl (1,1-dimethylethyl)carbamate), the active ingredient of Tandex weed and brush killer (FMC Corp.), is a nonselective broad spectrum herbicide. It is especially suited for the control of annual and hard-to-kill perennial broad-leaved weeds, and grasses, and woody species on noncrop land. Its most common uses are on railroad rights-of-way, airports, runways, industrial sites, and along fence lines.

Karbutilate is useful in controlling mesquite (*Prosopis* spp.) and other perennials that occur on extensive areas of grazing land. The applied karbutilate is carried by rainfall into the soil under the immediate area of application. Once in the soil, karbutilate is not susceptible to lateral movement. The brush will be killed when its extensive root system comes in contact with karbutilate. Only the grass in the immediate area of treatment will be affected. Before Tandex weed and brush killer could be used for the control of brushy species on rangeland, residue levels of karbutilate and its breakdown products available in the soil and in grass for ingestion by grazing livestock following application to rangeland had to be determined.

Karbutilate is metabolized in soil and grass to monomethyl karbutilate (II) (3-[[(methylamino)carbonyl]-amino]phenyl (1,1-dimethylethyl)carbamate) and demethyl karbutilate (III) (3-[(aminocarbonyl)amino]phenyl (1,1-dimethylethyl)carbamate) (Brandau and Robinson, 1974; Munger and Robinson, 1974). In water it is hydrolyzed to *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea (IV).

Karbutilate is the only urea carbamate herbicide commercially available. Gas chromatographic conditions for urea carbamates are not available. The gas chromatographic analysis of carbamates has been investigated by many and was recently reviewed (Magallona, 1975). Most workers agree that the gas chromatography of many carbamates cannot be carried out on the intact carbamates because of their thermal instability. Many authors have studied the direct gas chromatographic analysis of urea herbicides (McKone and Hance, 1968; Reiser, 1964; Henkel, 1966; Katz and Strusz, 1969; Spengler and Hamroll, 1970; Buser and Grolimund, 1974). Reiser states that only alkyl-substituted ureas can be chromatographed without decomposition. Henkel, Spengler, and Hamroll are of the opinion that most *N*-phenylurea compounds cannot be chromatographed undecomposed without previous chemical alteration. These compounds undergo thermal decomposition at the necessarily high temperatures in the injector block or the column.



I

II

III

IV

Work has been reported on the gas chromatographic analysis of certain carbamates and urea herbicides by derivatization of their aniline moieties after hydrolysis (Kirkland, 1962; Gutenmann and Lisk, 1964, 1966) and by bromination (Thier, 1971; Harris and Whiteoak, 1972). Direct methylation of phenylurea herbicides has recently been reported (Tanaka and Wien, 1973; Cochrane and

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Greenhalgh, 1973; Lawrence and Laver, 1975).

The direct gas chromatographic determination of karbutilate and its major metabolites II and III cannot be accomplished because of their thermal instability. Hydrolysis of the substituted urea group will produce the same amine for I, II, and III. Methylation of the urea will also produce the same products for I, II, and III. Because the measurement of individual metabolites was required, a residue method based on high-pressure liquid chromatography (HPLC) was developed.

EXPERIMENTAL SECTION

Reagents. Chloroform (stabilized with 1% ethanol), ethyl acetate, and ethylene chloride all distilled in glass (Burdick and Jackson Laboratories, Muskegan, Mich.), absolute methanol, and anhydrous granular sodium sulfate (Fisher Scientific) were used as received. Florisil adsorbent was obtained from the Floridin Co. (Pittsburgh, Pa.) and its moisture content adjusted to 3% by weight. Analytical standards of karbutilate, monomethyl karbutilate, demethyl karbutilate, *N'*-(3-hydroxyphenyl)-*N*,*N*-dimethylurea, and *N'*-(3-hydroxyphenyl)-*N*-methylurea were supplied by the Agricultural Chemical Division, FMC Corporation, Middleport, N.Y.

Apparatus. The liquid chromatograph used was a Waters Associates Model ALC 202 equipped with an ultraviolet photometric detector operating at 254 nm and a Valco Model CV-6-UH Pa-C-20 sample injection valve with a 15-μL loop. A 30 cm × 6 mm i.d. prepacked microporasil column (Water's Associates) was used. Cleanup columns were glass, 20 mm i.d. × 400 mm long. A Beckman pH meter and an Ohaus moisture balance were also used.

Sample Preparation. Soil samples were air dried for 48 h and ground in a mill. The samples were sieved through a number 10 (2.0 mm) screen to remove stones and homogenized by thorough mixing in a twin shell blender.

Grass samples were chopped in a Hobart food chopper. The moisture content of each sample was determined on the moisture balance.

Preparation of Water Extract for HPLC Analysis. A 200-mL sample of water was adjusted to pH 5 with hydrochloric acid and extracted twice with 200 mL of ethyl acetate. The ethyl acetate extract was concentrated to approximately 5 mL on a rotary evaporator and quantitatively transferred to a graduated test tube. The extract was concentrated to 1 mL using a gentle stream of nitrogen and was ready for HPLC analysis.

Preparation of Soil Extract for HPLC Analysis. A 100-g dry weight soil sample was placed in a blender jar with 100 mL of methanol and 50 mL of distilled deionized water. The sample was blended for 3 min at high speed and then transferred to a 250-mL centrifuge bottle. The sample was centrifuged for 20 min at 6000 rpm. The water/methanol mixture was decanted into a graduated cylinder and the volume recorded. The water/methanol solution was filtered through a 1-μm Nucleopore filter using a Millipore filter holder connected to a 500-mL Erlenmeyer flask and a water pump. The filtrate was transferred to a 1000-mL separatory funnel and extracted twice with 150 mL of chloroform. The chloroform extract was dried over sodium sulfate, filtered, concentrated to about 5 mL on a rotary evaporator, and quantitatively transferred to a graduated test tube. The extract was concentrated to 1 mL using a gentle stream of nitrogen and was ready for HPLC analysis.

Preparation of Grass Extract for HPLC Analysis. A 25-g equivalent dry weight grass sample was added to a blender jar. A ratio of 4 mL of water and 8 mL of methanol for every gram of dry grass was also added to the blender. The mixture was blended for 3 min at high speed and filtered through a Büchner funnel connected to an Erlenmeyer flask and a water pump. The volume of the solution was measured using a graduated cylinder. The water/methanol mixture was transferred to a separatory funnel and extracted with chloroform as described for soil extraction. After concentration, the chloroform extract was transferred to the cleanup column described below.

Cleanup Column. A cleanup column was prepared by adding to a glass column in the following order: a glass wool plug, 5 g of sodium sulfate, 10 g of Florisil (3% moisture), and a further 5 g of sodium sulfate. The Florisil column was prewet with 50 mL of chloroform. The concentrated grass extract was transferred to the column and allowed to elute dropwise. The column was washed with 100 mL of chloroform and the eluate discarded. The column was then eluted with 300 mL of 5% ethanol in chloroform (v/v) and this eluate (eluate A) concentrated on a rotary evaporator to 5 mL. The column was finally eluted with 300 mL of 20% ethanol in chloroform (v/v) and this eluate (eluate B) concentrated to about 5 mL on a rotary evaporator and transferred to a graduated test tube.

Hydrolysis and Cleanup for Grass. Eluate A was concentrated to dryness in a round-bottomed flask using a gentle stream of nitrogen. About 25 mL of 0.1 N sodium hydroxide was then added to the flask and the mixture allowed to stand at room temperature for 30 min, swirling the flask from time to time. The sodium hydroxide solution was then extracted twice with 25 mL of methylene chloride and the methylene chloride discarded. The aqueous phase was adjusted to pH 5 using hydrochloric acid. The solution was extracted twice with 25 mL of ethyl acetate, concentrated to about 5 mL, and added to a Florisil cleanup column identical with the one previously described. The column was washed with 200 mL of ethyl acetate and then eluted with 300 mL of 15% ethanol in chloroform (v/v). The eluate was concentrated on a rotary evaporator to about 5 mL and transferred to a graduated centrifuge tube. The extract was concentrated to 1 mL using a gentle stream of nitrogen and was ready for HPLC analysis.

Liquid Chromatographic Analysis. Quantitative determinations of karbutilate, monomethyl karbutilate, demethyl karbutilate, and *N'*-(3-hydroxyphenyl)-*N*,*N*-dimethylurea after extraction and cleanup were conducted by a high-speed liquid chromatograph operating under the following conditions: column, Microporasil (Water's Associates), 30 cm; column temperature, ambient; flow rate, 2.4 mL/min; detector, ultraviolet photometric detector operating at 254 nm; pressure, about 1000 psi; chart speed, 0.2 in./min. Three mobile phases were used—(a) 3% v/v absolute ethanol in dichloroethane; with the instrument equilibrated under these conditions, the retention times of karbutilate, monomethyl karbutilate, and *N'*-(3-hydroxyphenyl)-*N*,*N*-dimethylurea were 3.8, 5, and 4.5 min, respectively; (b) 7% absolute ethanol in dichloroethane; with the instrument equilibrated under these conditions, the retention time of demethyl karbutilate was 7.8 min; (c) 3% ethanol–10% acetonitrile in ethylene chloride; with the instrument equilibrated under these conditions, the retention times for *N'*-(3-hydroxyphenyl)-*N*,*N*-dimethylurea and *N'*-(3-hydroxyphenyl)-*N*-methylurea were 3.5 and 5.3 min, respectively.

Calculations are based on calibration factors obtained by dividing the amount of standard injected (micrograms)

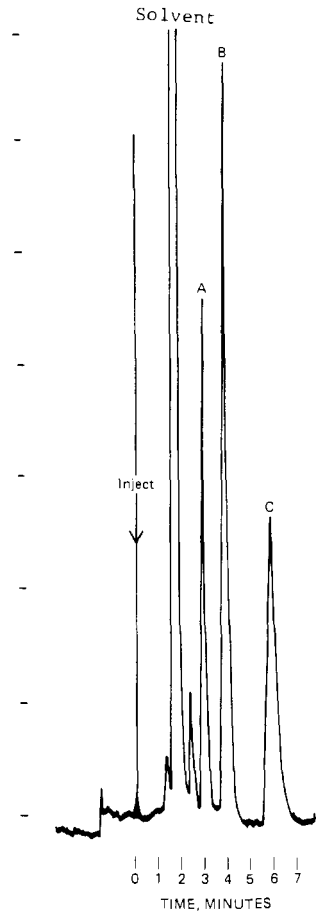

Figure 1. Liquid chromatogram of a mixture of 300 ng each of (A) karbutilate, (B) *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea, and (C) monomethyl karbutilate, on a 30 cm × 6 mm microporasil column: mobile phase, 3% ethanol/ethylene chloride; flow rate, 2.4 mL/min, pressure, ~1000 psi; ambient column temperature; UV detector, 254 nm; 0.02 absorbance full scale.

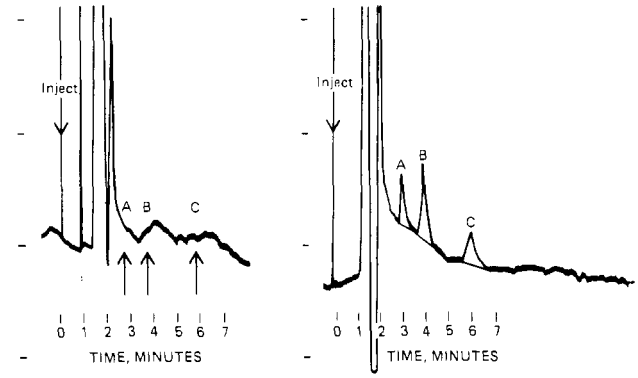

Figure 2. Analysis of untreated and fortified water. Fortification level of karbutilate (A) and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea (B), 0.01 ppm, monomethyl karbutilate (C), 0.02 ppm. Conditions are the same as in Figure 2.

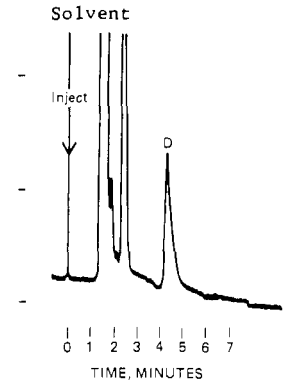

Figure 3. Liquid chromatogram of 300 ng of demethyl karbutilate (D) on 30 cm × 6 mm microporasil column: mobile phase 7% ethanol/ethylene chloride; flow rate, 2.4 mL/min; pressure, 1000 psi; ambient column temperature; UV detector, 254 nm; 0.04 absorbance full scale.

by the peak height (millimeters) obtained. The calibration factors are obtained by chromatographing 0.2 or 0.4 μg of compound. Since a plot of peak height vs. amounts injected is linear, a single calibration point in the form of a calibration factor is satisfactory for the calibration. Calibration factors were determined daily.

The following formula was used to determine the residue in parts per million for parent and breakdown products in water and in soil and for demethyl karbutilate in grass:

$$\text{ppm of residue} = [(\text{total } \mu\text{g of compd found})A]/S$$

where A = aliquot factor ([water/methanol decanted (mL)]/150 mL) and S = sample weight in grams. For grass, the total micrograms of carbamate is calculated by multiplying the total number of micrograms of the corresponding phenol by the molecular weight ratio of 1.59 for karbutilate and 1.64 for monomethyl karbutilate.

RESULTS AND DISCUSSION

The liquid chromatographic method described here permits good resolution and sensitivity for karbutilate and its metabolites. For analysis of residues in water, karbutilate, monomethyl karbutilate, and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea were all determined intact by one liquid chromatographic injection.

Figure 1 shows a chromatogram of a mixture of the three compounds obtained by the described chromatographic procedure. Figure 2 shows chromatograms of an extract

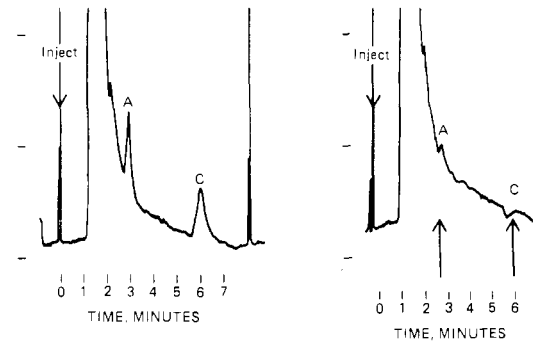

Figure 4. Analysis of untreated and fortified soil. Fortification levels of 0.1 ppm and 0.2 ppm for karbutilate (A) and monomethyl karbutilate (C), respectively. Conditions are the same as in Figure 2.

from water and an extract from the same water fortified with karbutilate, monomethyl karbutilate, and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea. Recoveries of karbutilate, monomethyl karbutilate, and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea averaged 89.4, 101.8, and 91.7%, respectively (Table I). The lower limit of detection of the method is 0.01 ppm for karbutilate and *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and 0.02 ppm for monomethyl karbutilate.

For residue analysis of soil, karbutilate and monomethyl karbutilate were determined intact in one liquid chromatographic scan and demethyl karbutilate in a second

Table I. Recovery of Karbutilate, Monomethyl Karbutilate, and *N'*-(3-Hydroxyphenyl)-*N,N*-dimethylurea from Water

Fortification level, ppm			% recovery		
Karbutilate	Monomethyl karbutilate	*N'*-(3-Hydroxyphenyl)-*N,N*-dimethylurea	Karbutilate	Monomethyl karbutilate	*N'*-(3-Hydroxyphenyl)-*N,N*-dimethylurea
0.01	0.02	0.01	82.5	96.3	76
0.01	0.02	0.01	93	98	117.3
0.02	0.04	0.02	89.1	89.9	94.5
0.03	0.06	0.03	87.8	110.4	88.7
0.04	0.08	0.04	106	135.6	96.3
0.06	0.1	0.06	89.1	89.7	84.0
1	2	1	84.3	93.6	86.4
1	2	1	84.6	98.5	88.8
2		2	89.9		108.5
2		2	88.1		76.2
		Av	89.4	101.8	91.7

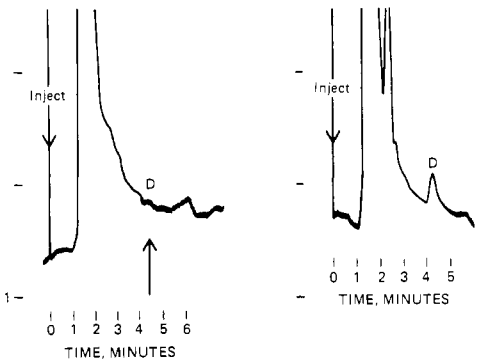

Figure 5. Analysis of untreated and fortified soil. Fortification level of 0.2 ppm of demethyl karbutilate. Conditions are the same as in Figure 4.

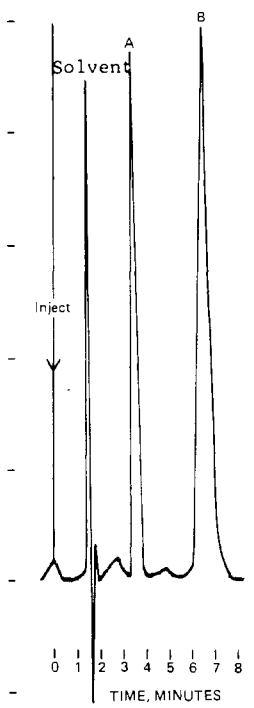

Figure 6. Liquid chromatogram of a mixture of (A) 150 ng of *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and (B) 300 ng of *N'*-(3-hydroxyphenyl)-*N*-methylurea on a 30 cm × 6 mm microporasil column: mobile phase, 3% ethanol/10% acetonitrile in ethylene chloride; flow rate, 2.4 mL/min; pressure, ~1000 psi; ambient column temperature; UV detector, 254 nm; 0.04 absorbance full scale.

liquid chromatographic scan with a different eluent. Figure 3 shows a chromatogram of demethyl karbutilate obtained by the described chromatographic procedure.

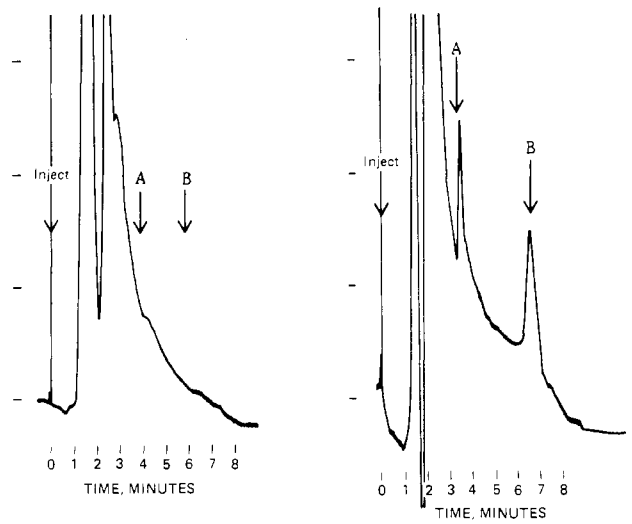

Figure 7. Analysis of untreated and fortified grass. Fortification level: karbutilate, 0.1 ppm; monomethyl karbutilate, 0.2 ppm. Peak A represents *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and peak B *N'*-(3-hydroxyphenyl)-*N*-methylurea. Conditions are the same as for Figure 7.

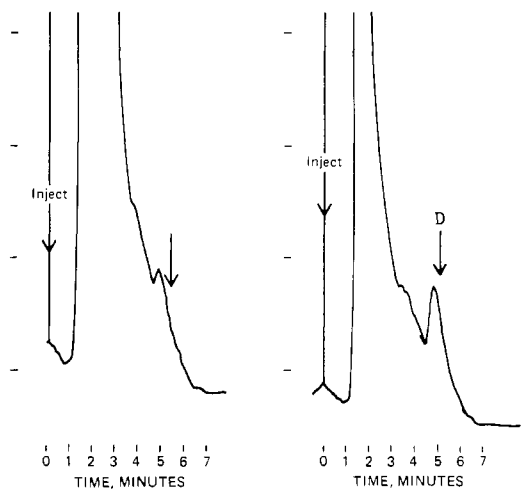

Figure 8. Analysis of untreated and fortified grass. Fortification level demethyl karbutilate (D), 0.2 ppm. Conditions are the same as for Figure 4.

Figures 4 and 5 show chromatograms of extracts from untreated soil and soil fortified with karbutilate, monomethyl karbutilate, and demethyl karbutilate. Recoveries of karbutilate, monomethyl karbutilate, and demethyl karbutilate averaged 95.1, 85.0, and 84.0%, respectively, on three different types of soils (Table II). Because of

Table II. Recovery of Karbutilate, Monomethyl Karbutilate, and Demethyl Karbutilate from Soil

Fortification level, ppm			% recovery		
Karbutilate	Monomethyl karbutilate	Demethyl karbutilate	Karbutilate	Monomethyl karbutilate	Demethyl karbutilate
Sandy loam soil					
0.1	0.2	0.2	84.5	93.8	99.9
0.1	0.2	0.2	118	123.3	91.5
0.2	0.4	0.4	100.1	101.3	79.3
0.2	0.4	0.4	91.7	105	61.4
0.3	0.2	0.2	82.8	79.9	78.8
0.5	0.4	0.4	73.7	93.2	81.3
0.8	0.6	0.6	86.8	98.3	86.1
1.0	0.8	0.8	94.5	98.3	78.4
1.5	1.0	1.0	84.0	80.3	84.9
3.0	1.2	1.2	80.8	73.8	79.5
5.0	1.4		88.3	103.9	
10	1.6		84.6	83.6	
25	0.8		103.1	76.4	
50	1.0		106.9	79.2	
300	0.6		100.8	78.0	
		Av % recovery	92.1	91.2	82.1
Silt loam					
1.0	0.4	0.2	106.6	76.5	85.3
10	0.6	0.3	99.8	82.4	88.9
25	0.8	0.3	103.1	76.4	74.4
50	1.0	0.4	106.9	79.2	90.1
300	0.6	0.4	100.8	78.0	92.3
		Av % recovery	103.4	78.5	86.2
Clay loam					
0.1	0.2	0.2	97.9	101.9	80.4
50	1.0	1.0	101.1	82.1	96.3
100	0.8		89.0	80.2	
400	0.3		96.5	91.5	
		Av % recovery	96.1	88.9	88.4
		Av % recovery for different soil	95.1	85.0	84.0

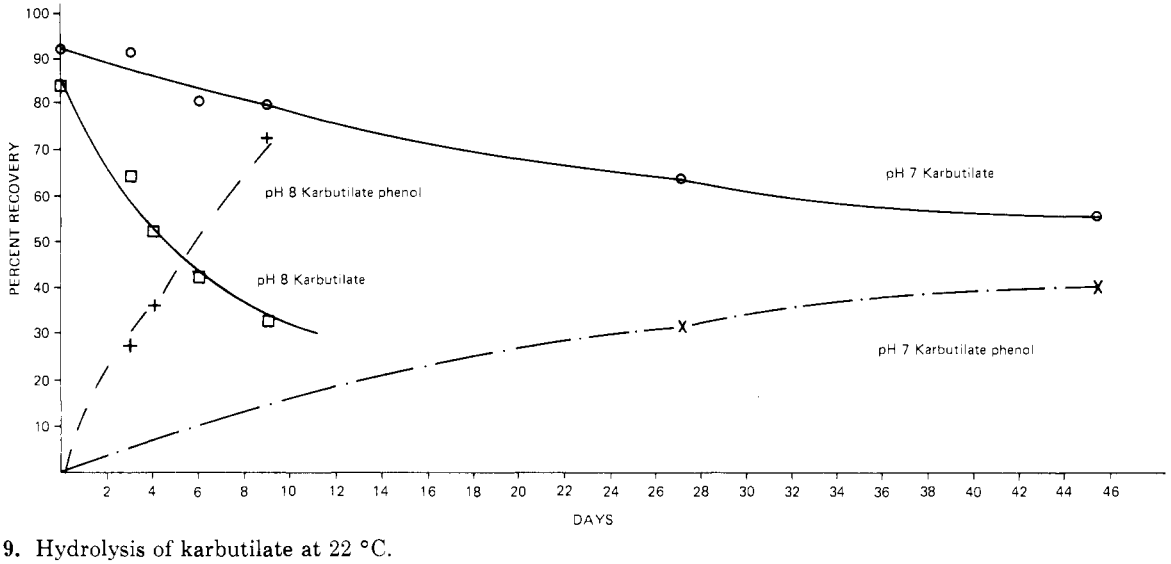

Figure 9. Hydrolysis of karbutilate at 22 °C.

the much longer retention of demethyl karbutilate on the adsorption column, solvent programming or two separate injections were necessary. Figure 6 represents a chromatogram of a mixture of *N'*-(3-hydroxyphenyl)-*N,N*-dimethylurea and *N'*-(3-hydroxyphenyl)-*N*-methylurea obtained by the described chromatographic procedure. Figures 7 and 8 show chromatograms of extracts of grass fortified with karbutilate, monomethyl karbutilate, and demethyl karbutilate. Recoveries of karbutilate, monomethyl karbutilate, and demethyl karbutilate from grass averaged 87.3, 79.8, and 83.2%, respectively (Table III). The lower limit of detection of the method for soil and grass is 0.1 ppm for karbutilate and 0.2 ppm for monomethyl karbutilate and demethyl karbutilate.

In soil, the major extractable metabolites of karbutilate are the products of demethylation, namely monomethyl karbutilate, which is further demethylated to demethyl karbutilate. Phenolic metabolites, which account for less than 20% of the residue, were present in the form of bound residue (Brandau and Robinson, 1974).

In the procedure for residues in soil, the extraction of karbutilate and its carbamate metabolites from soil with water/methanol effectively isolated those residues. No cleanup column was necessary. Karbutilate, monomethyl karbutilate, and demethyl karbutilate were determined intact. The completeness of extraction of karbutilate and

Table III. Recovery of Karbutilate, Monomethyl Karbutilate, and Demethyl Karbutilate from Grass

Fortification level, ppm			% recovery		
Karbutilate	Monomethyl karbutilate	Demethyl karbutilate	Karbutilate	Monomethyl karbutilate	Demethyl karbutilate
0.3	0.4	0.4	88.8	76.1	82.3
0.4	0.5	0.5	93.3	88.1	86.2
0.5	0.6	0.6	83.9	80.5	79.7
0.6	0.7	0.7	83.0	74.1	84.6
		Av	87.3	79.8	83.2

its metabolites was confirmed by studies involving field soils treated with radiolabeled karbutilate (Brandau and Robinson, 1974). The liquid chromatographic method for residues in soil was not applicable to the determination of residues in grass. The chloroform extract from plant substrates contained too many interfering materials.

The detector used (UV 254 nm) is not specific or selective for karbutilate and its breakdown products, since many compounds will absorb at 254 nm. Karbutilate and its breakdown products have a small absorption band at 254 nm. A very rigorous cleanup was needed to eliminate extractable interference from grass. Because of its low polarity, karbutilate is difficult to separate from nonpolar plant material. The nonpolar plant materials are not retained by the LC column but will elute with the liquid chromatographic solvent front and interfere with karbutilate.

The direct residue analysis of karbutilate and monomethyl karbutilate in grass is not simple. An alternative to analyzing for karbutilate is to change its structure. Hydrolysis of the carbamate to the phenol is the simplest method. This conversion, when used with high-speed liquid chromatography, has several advantages. The phenols are more polar than the carbamates and thus are retained longer on the LC column. The difference in HPLC retention time between the phenols is less than that of the corresponding carbamates.

The UV response of the phenol is at least as good as that of the carbamate so there is no loss in sensitivity. An acid–base partition of the phenol eliminates a very large number of nonpolar interferences. A more selective liquid chromatographic column could be used. In our work, an adsorption column was used but an ion exchange column could also be used and might provide more selectivity in the separation of interferences.

Although one Florisil cleanup column followed by the hydrolysis to the phenol was sufficient for most grass samples, a few samples, particularly the very wet samples, were not adequately cleaned and a second cleanup column was necessary. The difference in polarity between *N'*-(3-hydroxyphenyl)-*N*,*N*-dimethylurea and *N'*-(3-hydroxyphenyl)-*N*-methylurea is less than that between the respective parent compounds. A florisil cleanup column for the two phenols was easier to develop.

Demethyl karbutilate is the most polar metabolite. There was no need to hydrolyze it to the phenol after the first cleanup column since no interferences were observed. In neutral or alkaline water, karbutilate is quantitatively hydrolyzed to the corresponding phenol. After 45 days at 22 °C and pH 7, 45% of karbutilate remains. At pH 8, the half-life of karbutilate is 4.6 days (Figure 9).

This study shows the usefulness of high-pressure liquid chromatography for conducting sensitive analysis of pesticide residues that cannot be analyzed by gas chromatographic procedures. It also shows that the conversion of carbamate to the phenol offers many advantages when used with HPLC.

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