Analysis of Some Carbamate and Urea Herbicides in Foods by Gas–Liquid Chromatography after Alkylation

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The quantitative analysis of a number of carbamate and urea herbicides in selected foods was examined. The compounds were extracted from the crops with ethanol which was subsequently partitioned between water and chloroform. The organic extract was evaporated to dryness and alkylated with sodium hydride–methyl iodide. The products were extracted with hexane and directly analyzed by gas chromatography. Detection of the derivatives was accomplished with a Coulson electrolytic conductivity detector in the nitrogen mode. No column cleanup was required for any of the samples down to the 0.01 ppm level. Detection limits were about 0.005 ppm. Recoveries were usually 60–100% depending upon the herbicide. Confirmation of the chlorine-containing herbicides was carried out with the Coulson in the chloride (reductive) mode.

The direct gas chromatographic analysis of carbamate and urea herbicides has been carried out by a number of authors (Fishbein and Zielinski, 1965; McKone and Hance, 1968; Onley and Yip, 1971; Katz and Strusz, 1969; Spengler and Hamroll, 1970; Buser and Grolimund, 1974). Although different columns and GLC conditions were used, these authors generally agree that for good separations and reproducible analyses of such compounds, operational parameters must be rigidly controlled. Unfortunately, when doing sample analysis such restrictions often make direct determinations impossible due to interferences which cannot be avoided by remaining within the required GLC settings. Many workers prefer to analyze these herbicides as GLC stable derivatives. Normally, these derivatives are chosen to permit analyses over a wide range of GLC conditions with no decomposition. Work has been reported on the analysis of carbamate and urea herbicides by derivatization of their aniline moieties after hydrolysis (Kirkland, 1972; Lisk, 1964; Gutenmann and Lisk, 1966) and by bromination (Thier, 1971; Harris and Whiteoak, 1972). Direct alkylation of phenylurea herbicides has recently been reported (Tanaka and Wien, 1973; Cochrane and Greenhalgh, 1973). Tanaka and Wien (1973) used flash-heater methylation with trimethylanilinium hydroxide (methelute) to produce the 3-N-methyl analog of several ureas. This on-column alkylation technique required a minimum of 1 μg of herbicide injected for reliable results. For comparison purposes they synthesized the methylated products with NaH–methyl iodide. Cochrane and Greenhalgh (1973) examined NaH–methyl iodide alkylation for application to residue size samples of urea herbicides and other pesticides with alkali flame ionization detection. These authors found that the alkylated products were far superior to the parent compounds for GLC purposes. Gas chromatography could be carried out at a wide variety of temperatures on a number of different columns with no decomposition. This same alkylation reaction was carried out by Lawrence (1974) for the confirmation of triazine herbicides in crops using electrolytic conductivity detection. The analysis of two diazinon metabolites in urine has also been examined with this alkylation technique (Lawrence and Iverson, 1975). NaH–methyl iodide is well suited to derivatization and GLC with electrolytic conductivity detection in the nitrogen mode since none of the reagents or solvents used contains nitrogen. Thus, no interferences are observed other than the pesticide reaction products. The present work reports on the use of the NaH–methyl iodide alkylation reaction for the quantitative analysis of carbamate and urea herbicides in selected foods by GLC with nitrogen specific detection.

EXPERIMENTAL SECTION

Apparatus. An Aerograph Model 600C gas chromatograph equipped with a Coulson conductivity detector (Tracor Inc., Austin, Tex.) in the nitrogen mode was used for the study. A 2 m × 6 mm o.d. coiled glass column was packed with 4% SE 30/6% QF1 on Chromosorb WHP (80–100 mesh). Operating conditions were: pyrolysis furnace temperature, 780 °C; transfer unit, 210 °C; helium carrier, 60 ml/min; helium sweep, 60 ml/min; hydrogen, 50 ml/min; dc bridge potential, 30 V. Column temperature was varied for the different samples analyzed. The GLC effluent was vented to the atmosphere for 1–2 min after injection before being directed to the Coulson furnace. The reservoir water level was maintained 1 cm above the pump entrance. A 0.004 in. diameter stainless steel wire was inserted into the distilled water entrance of the Coulson cell (Lawrence and Sen, 1975). This insertion improved sensitivity of the Coulson two- to threefold.

Reagents. The sodium hydride (Baker, Phillipsburg, N.J.) obtained in a 50% oil dispersion was washed with hexane before use. Dimethyl sulfoxide (B.D.H., Poole, England), methyl iodide (Fisher, Pittsburgh, Pa.), and all other reagents were used as obtained from the suppliers. All solvents were glass-distilled pesticide-grade materials. The phenylureas studied were: linuron (N-methyl-N-methoxy-N'-(3,4-dichloro)phenylurea), monuron (N,N-dimethyl-N'-(4-chloro)phenylurea), diuron (N,N-dimethyl-N'-(3,4-dichloro)phenylurea), fluometuron (N,N-dimethyl-N'-(3-trifluoromethyl)phenylurea), chloroxuron (N,N-dimethyl-N'-(4-chlorophenoxy)phenylurea), fenuron (N,N-dimethyl-N'-phenylurea), and chlorbromuron (N-methyl-N-methoxy-N'-(3-chloro-4-bromo)phenylurea). The phenylcarbamates examined were propham (isopropyl N-phenylcarbamate), chlorpropham (isopropyl-N-(3-chloro) phenylcarbamate), and swep (methyl-N-(3,4-dichloro) phenylcarbamate). Solutions of these were prepared in methanol for spiking purposes and in acetone for calibration curve formation. The crops examined were potatoes, carrots, peas, oranges, asparagus, spinach, pineapple, and corn.

Sample Extraction. The sample (100 g) was blended (Waring Blendor) with 10 g of Celite 545 and 200 ml of ethanol for 4–5 min. The extract was filtered through a 600-ml medium porosity sintered glass funnel. The filter cake was then rinsed with 50 ml of ethanol. The collected filtrate was added to a 1-l. separatory funnel containing 500 ml of doubly distilled water and 50 ml of chloroform. The mixture was gently shaken for about 2 min and the chloroform collected. The aqueous layer was extracted twice more with 50-ml volumes of chloroform. The combined organic phases

were dried with $MgSO_4$ (about 5 g). The dry extract was filtered through a 250-ml medium porosity sintered glass funnel into a 250-ml round-bottomed flask (to remove small $MgSO_4$ particles) and taken to dryness by rotary vacuum evaporation at 30 °C. The residue was transferred to a 20-ml test tube with Teflon-lined screw cap and evaporated to dryness at 30 °C under a stream of nitrogen.

Alkylation. To the residue in the test tube were added 0.5 ml of Me_2SO and 0.5 ml of benzene followed by 0.5 ml of CH_3I and about 20–50 mg of NaH. The capped test tube was gently shaken in a horizontal mechanical shaker for 15 min at room temperature. After this time, 3.0 ml of hexane was added and the contents shaken by hand for 30 sec. Ten milliliters of distilled water was carefully added dropwise to the reaction mixture to destroy the excess NaH. (Care must be·taken in this step since NaH reacts rapidly with water to produce hydrogen gas.) After evolution of hydrogen ceased the tube was then capped and vigorously shaken for 30 sec. The layers were permitted to separate (with centrifugation at 2000 rpm if required) and an aliquot of the hexane layer was injected into the gas chromatograph for analysis. For calibration purposes and recovery studies, standards were carried through the same alkylation procedure.

RESULTS AND DISCUSSION

Alkylation. The reaction scheme for the alkylation of the herbicides is shown for linuron. The strong base is re-
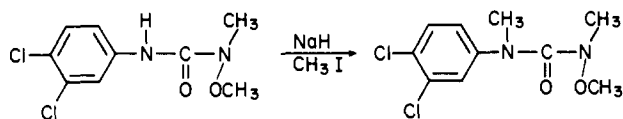
Linuron   Methylated Linuron

quired to remove the proton from the nitrogen atom to form the anion of the herbicide. This then reacts with the methyl iodide to yield the derivative. The percent yield was consistent for each compound and was 80–100% for the different herbicides examined. The alkylated product was verified by mass spectrometry. Dimethyl sulfoxide (Me_2SO) was the preferred solvent for the reaction. Dimethylformamide–tetrahydrofuran (Tanaka and Wien, 1973) was found less desirable because of the solvent front observed after venting due to the nitrogen-containing dimethylformamide. This could not be removed upon partitioning. Thus, Me_2SO was chosen for the reaction.

The addition of 1 ml of benzene to the test tube before the Me_2SO readily dissolved the residue and provided improved reproducibility, since frequently much of the crop residue would not dissolve when using Me_2SO alone. Benzene had no significant effect on the alkylation. The volume of methyl iodide in the reaction was not critical above 0.1 ml. Lower quantities caused poorer reproducibilities, possibly due to the high volatility of the CH_3I. The amount of NaH added was found to influence the alkylation rate. For the herbicides studied 20–40 mg of the base provided maximum yield of products.

Extraction of the products from the reaction mixture was quantitative with 3 ml of hexane. The total volume of the organic phase was ≃4 ml due to the benzene and CH_3I present in the reaction mixture. The Me_2SO remained in the aqueous layer and was thus not injected into the gas chromatograph. Several other extracting solvents such as chloroform, ethyl acetate, benzene, and ether were examined. All solvents quantitatively recovered the alkylated products from the reaction mixture. Hexane or benzene was preferred because of their low solubility for water and Me_2SO.

Chromatography. Figure 1 shows a chromatogram of a number of alkylated carbamate and urea herbicides on 4% SE 30/6% QF1 at 199 °C. Table I lists the retention times
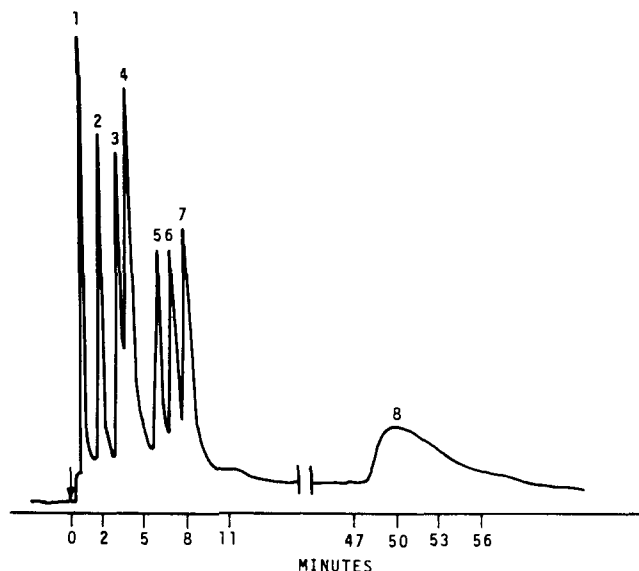

Figure 1. Gas chromatogram of several alkylated herbicides. About 50–100 ng of each was injected. Coulson attenuation 16X: (1) propham; (2) chlorpropham; (3) swep; (4) monuron; (5) linuron; (6) diuron; (7) chlorbromuron; (8) chloroxuron. Coulson vented 30 sec after injection.

Table I. Alkylated Product Retention Times[a]

Herbicide	t_R of alkylated product, min
Propham	1:16
Fluometuron	1:58
Chlorpropham	2:09
Fenuron	2:12
Swep	3:32
Monuron	4:06
Linuron	6:17
Diuron	7:16
Chlorbromuron	7:55
Chloroxuron	50:00

[a] Column temperature, 199 °C; flow rate, 100 ml/min; 4% SE 30/6% QF1.

of the alkylated herbicides examined. Attempts were not made to separate all of the derivatives from one another. Several column liquid phases have been examined for such purposes by Tanaka and Wien (1973). A temperature of 223 °C was used for chloroxuron determinations, which reduced the retention to about 12 min.

The sensitivity of the alkylated products varied with the herbicides. Linuron was about half as sensitive as monuron when identical quantities were reacted. This is due partially to the higher molecular weight and longer retention time for linuron. Another possible source is that the alkylation reaction does not produce the same yields with all herbicides studied. Most herbicides, however, had sensitivities between linuron and monuron. Detection limits at a 3:1 signal/noise ratio were about 1–2 ng of equivalent herbicide.

Sample Analysis. The developed sample extraction procedure was found satisfactory for the compounds and foods studied. Chloroform proved to be superior for partitioning of the herbicides from the aqueous ethanol, compared to the less polar solvents such as hexane or petroleum ether. Ethyl acetate and ether were considered unsatisfactory because the high solubility of water in these made drying difficult. Water must be completely removed from the residue before alkylation since this destroys the sodium hydride by
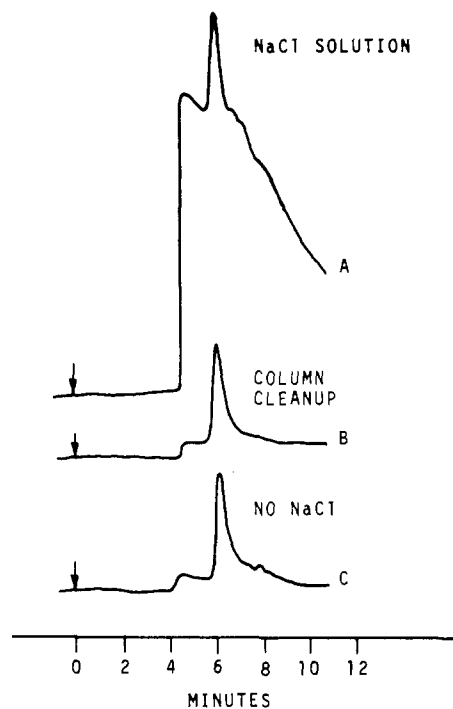
Figure 2. Chromatograms of linuron in potatoes at 0.1 ppm; 20 ng of equivalent linuron injected: (A) 10 ml of NaCl added to partition mixture; (B) same as A but with column cleanup; (C) same as A but with no NaCl solution added to partition step. Coulson vent closed at 4:00; attenuation 1X.

Figure 3. Typical chromatograms of herbicides spiked in several foods. Monuron, linuron, and diuron were added to the crops at the specified levels; M = monuron, L = linuron, D = diuron; 10 ng of equivalent herbicides was injected, 1X attenuation, except for the spinach where 5 ng was injected. Chromatograms were obtained on different days, under different conditions and thus are not comparable. (The 1.0-ppm potato sample was not spiked with monuron.)

conversion to sodium hydroxide which may cause some hydrolysis of the herbicides during the reaction.

The addition of 10 ml of saturated NaCl solution to the partitioning mixture was initially carried out to help force the herbicides into the chloroform; this addition also forced much coextractive material into the chloroform which ultimately resulted in background interference in the chromatograms. Figure 2 illustrates the differences in the chromatograms obtained with and without addition of NaCl solution in the partition step. The recoveries were not significantly improved by NaCl addition. Initially column cleanup was attempted to remove the background interference. The residue from the chloroform partition was added to a 4 in. column (1.5 cm diameter) of 2% deactivated Florisil and eluted successively with 50 ml of 10, 35, and 100% ether in petroleum ether. Linuron was quantitatively removed in the 35% fraction. The others studied (propham, monuron, and diuron) were eluted completely in the 100% ether fraction. This elution scheme removed the background interference caused by the NaCl addition (Figure 2B). For screening purposes at levels of 0.01 ppm or greater the column cleanup is unnecessary if no NaCl is added to the partition step.

All subsequent extraction and recovery studies were carried out with no NaCl and no column cleanup. Recoveries of three herbicides from the samples were not significantly affected by the crop type. Table II lists the recoveries of three herbicides from several of the crops examined. Figure 3 illustrates several chromatograms of the simultaneous extraction of linuron, monuron, and diuron from crops spiked at several levels. Spinach gave the worst interference of the crops studied. Spinach samples spiked at the 0.01-ppm level occasionally could not be analyzed due to high background.

Significant improvement was observed if the alkylated products were passed through a 2% deactivated Florisil column. The alkylated products were less polar than the parents and were completely removed with 50 ml of 10% acetone in hexane.
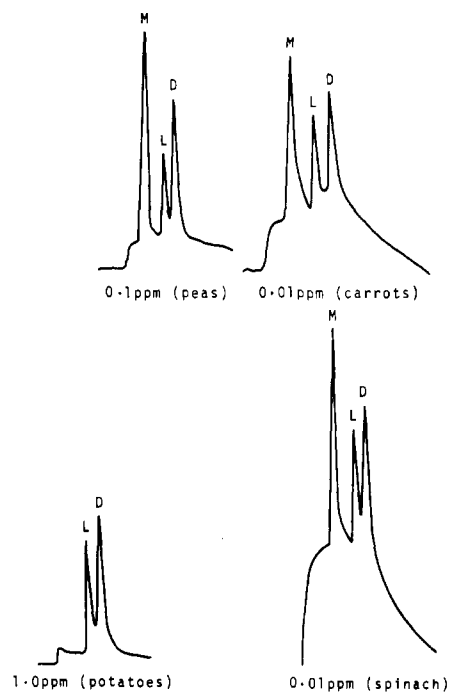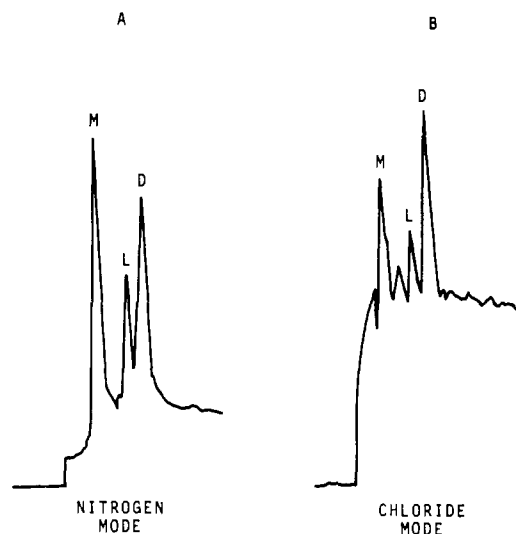

Figure 4. Comparison of nitrogen and chloride mode for asparagus analysis at 0.1 ppm: (A) nitrogen mode, 10 ng of equivalent herbicides injected (1X attenuation); (B) chloride mode, 25 ng of equivalent herbicides injected (8X attenuation); column, 2 m, 4% SE 30/6% QF1, 191 °C.

Confirmation. The Coulson was slightly more sensitive in the chloride mode than in the nitrogen mode to the herbicides. About 0.5–1 ng could be detected at a signal/noise ratio of 3:1. However, for sample analysis the chloride mode was much less satisfactory. High background was always observed and analysis of samples at 0.01 ppm was frequently impossible. The column cleanup mentioned above for the alkylated products improved analysis at these low levels. Figure 4 compares chromatograms of the same sample in the two Coulson modes without column cleanup. The chromatogram shown in Figure 4B was obtained after

Table II. Recovery Studies[a]

Herbicides	Potatoes			Carrots			Oranges, 0.1	Peas, 0.1	Corn, 1.0	Pine- apple, 0.1	Aspar- agus 0.1	Spinach	
	1.0	0.1	0.01	1.0	0.1	0.01						0.1	0.01
Linuron	99	97	100	92	98	96	100	98	98	93	98	102	100
Monuron	65	75	93	–	65	84	70	62	–	58	64	76	85
Diuron	81	84	95	–	78	98	84	87	74	68	80	95	100

[a] Percent recovery at indicated spiked values (in parts per million). Each value is the average of duplicate analyses. Dashes indicate that no analyses were performed.

evaporating the final extract to dryness to remove any CH_3I present and then redissolved in hexane. This treatment resulted in a lower background in the chloride mode. Other columns used to confirm in the chloride mode were 6% DC 200, 5% SP 525, and 5% OV 17. All of these proved satisfactory for direct confirmation at the 0.1-ppm level.

Bleeding of the liquid phases was found to cause some problems in the chloride mode. SE 30/QF1 gave a consistently high background and could not be used at the 1× attenuation. OV 17 gave the least interference. In general, any halogen-containing liquid phase should be avoided in the chloride mode. In the nitrogen mode no interferences were observed with SE 30/QF1 although QF1 contains fluorine. Use of this phase necessitated routine (once a month) replacement of the acid gas scrubber at the end of the pyrolysis tube.

CONCLUSION

The developed method was found promising for the routine screening, quantitation, and confirmation of most N-phenylcarbamate and N-phenylurea herbicides by GLC with electrolytic conductivity detection. Several hundred crop samples were passed through the GLC system without contamination of the pyrolysis tube or chromatography column.

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Photosensitization and Luminescence of Picloram

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The photosensitization of picloram (4-amino-3,5,6-trichloropicolinic acid) was studied with known triplet-energy sensitizers. Benzophenone and benzoate increased the rate of photodecomposition of picloram by factors of about 3 and 2, respectively, upon photolysis (313 nm) in aqueous solution (pH 9.3). The quantum yields for the disappearance of picloram (aerated) with 254- and 313-nm light were 0.037 and 0.04, respectively. Phosphorescence emission of picloram in EPA– glass at 77 K occurred at 450 nm with a radiative lifetime of 40 msec for the free acid and 32 msec for the methyl ester, thus indicating an n,π* triplet state. Fluorescence emission was quenched in weakly acidic, neutral, and basic solutions, but emitted strongly at 425 nm in aqueous sulfuric acid solutions at pH <1.16. The conclusion drawn from these results is that photodecomposition of picloram takes place from the excited triplet state.

Applications of picloram (4-amino-3,5,6-trichloropicolinic acid) to Texas' rangelands and forests have been effective in the control of a variety of undesirable woody plants and herbaceous weeds (Bovey and Scifres, 1971). Sensitive crops, such as soybeans, suffer detrimental effects from picloram in soils and residues transported by runoff water from treated areas. Picloram has been shown to photodecompose in aqueous solution in the laboratory by direct

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photolysis with 254 nm (Hall et al., 1968) and with ~366 nm (Mosier and Guenzi, 1973). The dechlorination of picloram appears to be the most clearly defined photochemical reaction that results from the photolysis of picloram. Hall et al. demonstrated and Mosier and Guenzi later confirmed that two chloride ions are liberated for each molecule of picloram that undergoes photodecomposition. Very little success has been obtained in isolating and identifying photoproducts of picloram, thus limiting the mechanistic characterization of the degradation process. A better knowledge of its photochemical degradation is necessary to fully assess the fate of picloram and its photoproducts in the aquatic environment.