Direct Analysis of Some Carbamate Pesticides in Foods by High-Pressure Liquid Chromatography

The application of high-pressure liquid chromatography (HPLC) to the screening of several carbamate pesticides in selected foods was investigated. The pesticides were extracted from crops (cabbage, corn, potato, and wheat) with acetone, and then partitioned into hexane–methylene chloride. The organic extract was reduced to a small volume and passed through a 2% deactivated Florisil column. The fraction containing the pesticides was evaporated to dryness and dissolved in isooctane for analysis by HPLC on a 25 cm × 2.8 mm i.d. column of LiChrosorb Si 60 (5 μm) with UV detection at 254 nm. Detection limits of 0.004–0.05 ppm were obtained for carbamates such as swep, carbaryl, zectran, matacil, and mobam while others such as landrin, carbofuran, and banol could be detected at 0.1–0.3 ppm.

The analysis of carbamate pesticides by high-pressure liquid chromatography (HPLC) has been carried out by a number of workers using several techniques. Direct HPLC of intact carbamates has been limited to standards (Seiber, 1974; Ishii and Otake, 1973; Thruston, 1972; Moye, 1975), formulations (Argauer and Warthen, 1975; Colvin et al., 1974), and water samples (Thruston, 1972). Little work has been done to date on the HPLC analysis of this class of compounds in foods at residue levels. Frei et al. (1974) formed fluorescent derivatives of the phenolic hydrolysis products of a number of carbamates and applied this technique to soil and water samples. The fluorescent derivatives were detectable in low parts per billion concentrations. Kirkland et al. (1973) determined benomyl (methyl 1-(butylcarbamoyl-2-benzimidazolecarbamate)) after conversion to methyl 2-benzimidazolecarbamate (MBC) in 19 types of plant tissues at levels of 0.1 ppm or less. A dynamic fluorogenic labeling technique described by Moye and St. John (1975) appears to be a selective and sensitive approach to multi-carbamate residue analysis. This technique involved post-column hydrolysis to methylamine which subsequently reacted with *o*-phthalaldehyde to form a fluorescent product. They reported good results at levels of 0.02–0.2 ppm for several methylcarbamates in cabbage, lettuce, and celery.

The approach taken in this work is to attempt to clean up samples sufficiently to screen for carbamate pesticides in foods directly by using UV detection at 254 nm. The detector is a readily available UV filter photometer. Chromatography is carried out on 5-μm silica gel with 5% 2-propanol in isooctane as mobile phase. The cleanup technique is designed to fit into a multi-pesticide residue method for which GLC has been used as the determinative step. This is part of a program to integrate HPLC with GLC for pesticide residue screening in foods.

EXPERIMENTAL SECTION

Apparatus. A Waters Associates Model 6000A pump was used for solvent delivery. A Waters Model 440 UV detector (254 nm) connected to a 1.0 mV recorder (rather than a 10 mV recorder as recommended in the manual) was used for detection of the pesticides. The chromatography column was 25 cm × 2.8 mm i.d. stainless steel, slurry packed with LiChrosorb Si 60 (5 μm). The mobile phase consisted of 5% 2-propanol in isooctane at 0.5–1.0 ml/min flow rate. Samples were injected via a modified sample loop injector (Cassidy, 1976) which allowed for syringe injection at ambient pressure.

Reagents. All solvents were glass-distilled, residue-free materials. The carbamates studied were carbaryl (1-naphthyl *N*-methylcarbamate), Mobam (4-benzothienyl *N*-methylcarbamate), aminocarb (4-dimethylamino-3-methylphenyl *N*-methylcarbamate), Zectran (4-dimethylamino-3,5-dimethylphenyl *N*-methylcarbamate), methiocarb (4-methylthio-3,5-dimethylphenyl *N*-methylcarbamate), propoxur (2-isopropoxyphenyl *N*-methylcarbamate), swep (methyl *N*-(3,4-dichlorophenyl)carbamate, carbofuran (7-(2,3-dihydro-2,2-dimethyl)benzofuranyl *N*-methylcarbamate), Landrin (3,4,5-trimethylphenyl *N*-methylcarbamate), and Banol (2-chloro-4,5-dimethylphenyl *N*-methylcarbamate). Stock solutions of these were prepared in 2-propanol (1 mg/ml) and diluted with isooctane for working standards. The crops examined were potato, corn, cabbage, wheat, and turnip, all purchased locally.

Table I. Retention Times and Sensitivities of Carbamates[a]

Carbamate	Retention time, min	Detectability[b]
Swep	9.0	0.13
Banol	10.4	40
Landrin	11.2	34
Zectran	11.5	1.0
Propoxur	12.5	3.5
Methiocarb	13.1	3.0
Carbaryl	16.5	0.9
Carbofuran	16.5	30
Mobam	19.0	0.3
Aminocarb	19.8	0.8

[a] Chromatographic conditions as described in the text. Flow rate 0.5 ml/min. [b] Nanograms required to produce a 2-cm peak at maximum sensitivity (0.0005 AUFS), 1.0 mV recorder, at retention times shown.

Sample Extraction. Spiked sample (35 g) was blended with 100 ml of acetone. The filtered extract was partitioned with methylene chloride–hexane (1:1) followed by further partition of the remaining aqueous layer with 2 × 70 ml of methylene chloride. The combined organic extracts were dried with sodium sulfate and reduced to near dryness for column chromatography on 2% deactivated Florisil. The carbamates were eluted completely with 100 ml of 15% acetone–hexane. This fraction was evaporated just to dryness and redissolved in isooctane for HPLC. Details of this procedure are described elsewhere (Lawrence, 1976).

RESULTS AND DISCUSSION

The UV detector used gave excellent sensitivity with extremely low noise. It was used routinely at maximum sensitivity (0.0005 AUFS, 1 mV recorder) producing 2% baseline noise and negligible long term drift. Table I lists the retention times and detectabilities of the carbamates studied. Carbaryl and carbofuran were not separated with this system. These may be separated by reversed-phase chromatography with Permaphase ODS as stationary

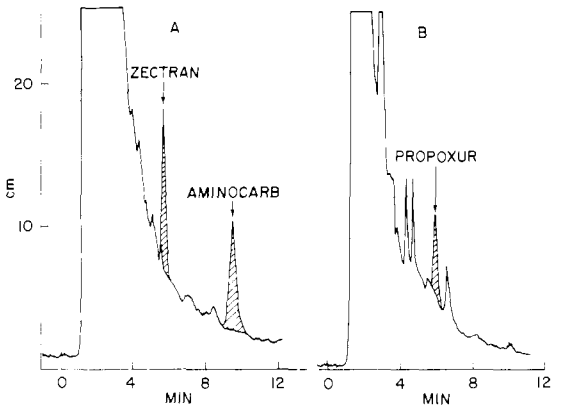

Figure 1. Chromatograms of: (A) Zectran and aminocarb in corn (0.1 ppm); 50 mg equiv of corn injected; (B) propoxur in cabbage (0.1 ppm); 100 mg equiv of cabbage injected; both chromatograms, 1.0 ml/min flow rate; 0.001 AUFS.

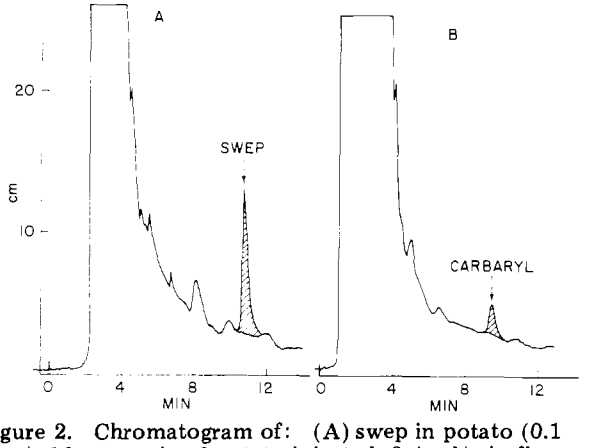

Figure 2. Chromatogram of: (A) swep in potato (0.1 ppm); 10 mg equiv of potato injected; 0.4 ml/min flow rate; 0.001 AUFS; (B) carbaryl in wheat (0.1 ppm); 50 mg equiv of wheat injected; 1.0 ml/min flow rate; 0.002 AUFS.

phase and 6% methanol–water as mobile phase (Thruston, 1972). However, work with this system on food samples has not been reported.

All carbamates studied were quantitatively eluted from the 2% deactivated Florisil column with 15% acetone–hexane. The extraction and Florisil cleanup were adequate for analysis of all of the carbamates at 0.1–0.3 ppm or less in the foods studied with the exception of wheat. A different cleanup or chromatography system would be required for this crop to reduce the large peak at the solvent front. Figures 1 and 2 show results of some carbamates spiked in several of the foods at 0.1 ppm. The cross-hatched areas represent the differences between chromatograms of spiked and blank (control) samples, i.e. the peaks due to the pesticides. Carbamates such as Zectran, aminocarb, propoxur, and swep were easily detected at this level. Figure 3 shows the chromatographic results of carbaryl and Mobam spiked in potato (0.02 ppm) and corn (0.004 ppm), respectively. The sensitivities of carbaryl and Mobam were such that these could be detected at 0.004–0.02 ppm in the foods studied (wheat

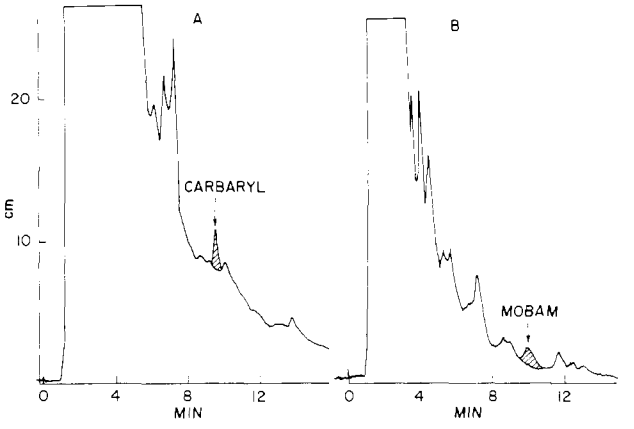

Figure 3. Chromatogram of: (A) carbaryl in potato (0.02 ppm); 140 mg equiv of potato injected; 1.0 ml/min flow rate; 0.001 AUFS; (B) Mobam in corn (0.004 ppm); 50 mg equiv of corn injected; 1.0 ml/min flow rate; 0.001 AUFS.

excepted). However, carbamates such as carbofuran, Landrin, Banol, and others of similar UV sensitivity at 254 nm (such as butacarb, meobal, and bux) were detected only at 0.1 ppm or greater.

Although no statistical treatment of the method or extensive recovery studies were carried out in this work, the approach appears suitable for quantitative analysis. Estimated recoveries were generally >70% at 0.1–1.0 ppm. Peak height and retention times were also very consistent with the modified syringe-loop injector used.

The described technique provides a rapid method for direct screening of several carbamate insecticides in a number of foodstuffs. No chemical reactions or specialized reagents are required. The method should be applicable to other carbamates in many different foods.

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