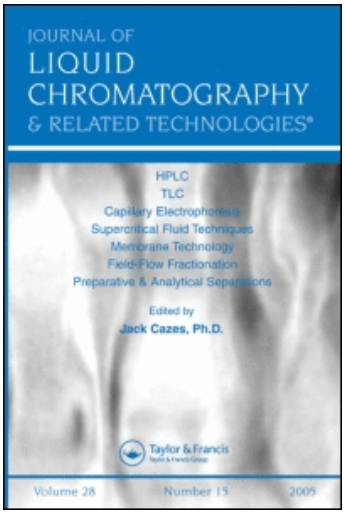

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AN INTERNAL STANDARD HPLC METHOD FOR THE ANALYSIS OF PROPOXUR

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ABSTRACT

An internal standard reversed phase hplc method for the analysis of propoxur is described. Analysis is accomplished in 15 minutes. The propoxur content is determined by comparing the response for the propoxur peak to the response of n-butyrophenone which is incorporporated as an internal standard. The analysis of a 2% rat bait is illustrated.

INTRODUCTION

Propoxur {2-(1-methylethoxy)phenol methylcarbamate, Baygon, Aprocarb} is a widely used carbamate pesticide with both contact and stomach poison activity (1). It has been long recognized that the gas chromatographic analysis of carbamates is at best a difficult task. If analytical conditions are not tightly monitored and controlled, severe thermal degradation may occur. Despite decomposition problems often encountered, carbamates such as propoxur have been successfully analyzed by gas chromatography (2-5). TLC methods have also been employed to analyze propoxur (6).

Recently it has been recognized that hplc may be a viable alternative to gc for the analysis of thermally unstable carbamates. The separation of carbamates from one another by hplc has been described and reviewed in several sources (7,8). The paper by Sparacino and Hines (7) describes both reversed phase and normal phase separations of a variety of carbamates including propoxur.

This paper describes a specific internal standard reversed phase hplc method for the analysis of propoxur. This method is useful for the rapid and accurate analysis of technical and formulated propoxur in a quality control or research laboratory.

EXPERIMENTAL

Solvents and Reagents

Methanol was obtained from Burdick and Jackson (Muskegon, Mich.). Water was distilled, deionized and passed through an activated carbon filter before use. All solvents were filtered and degassed before use. n-Butyrophenone (99%) was purchased from the Aldrich Chemical Co., Inc. (Milwaukee, Wisc.). Octadecyltriethoxysilane and trimethylchlorosilane were obtained from Silar Laboratories, Inc. (Scotia, NY).

Instrumentation

The liquid chromatograph employed in this study consisted of components purchased from Waters Associates (Milford, Mass.). Pumping was accomplished via two model 6000A pumps controlled by a model 660 solvent programmer. Injections (10 ul) were made via a model U6K valve and detection was accomplished by a model 440 absorbance detector at 280 nm with a sensitivity of 0.1 AUFS. Data were collected on an Omniscribe (Houston Instruments) recorder using a chart speed of 0.5 cm/min at 10 mv full scale deflection. The column employed was home-made. It consisted of a 25 cm L x 6mm ID body packed with a brush type octadecyl derivatized Partisil 5 phase. The mobile phase employed with this column was 35% methanol/65% water. The flow rate used was 0.8 ml/min for a pressure drop of 1,200 psi. Temperature was controlled at 40°C with a system described elsewhere (9).

Column Preparation

In a flask, 10 grams of Partisil 5, (Whatman, Inc.) previously stored under desiccation, was slurried in 50 ml of dry benzene. To this mixture, 0.84 g of Octadecyltriethoxysilane was added and the mixture was shaken for 2-1/2 hours at room temperature. The silica was then filtered and washed with benzene and placed in a solution consisting of 3 ml of trimethylchlorosilane in 50 ml of benzene. This mixture was allowed to react one hour. The derivatized silica was then filtered and washed with benzene, chloroform and methanol (3x50 ml each). The packing was allowed to air dry. A subsample of the packing was dried at 40°C under vacuum for three hours and submitted for carbon analysis. Analysis yielded 4.0% carbon bonded to the surface. Previous results (10-12) indicate this type of reaction condition generates essentially a brush type support with perhaps some patches of polymer. Details of bonded phase preparation schemes and factors effecting reactivity and surface coverage can be found in the review by Grushka and Kikta

(12) and the references therein. The column was packed from a methanol/ethylene glycol slurry using techniques described elsewhere (13).

Sample Preparation

A standard solution was prepared by dissolving 0.00893 g of 98% propoxur technical and 0.00514 g of n-butyrophenone in 10 ml of methanol. In order to analyze the rat bait, 0.48526 g of nominally 2% rat bait was weighed out and 0.00646 g of n-butyrophenone was added to it. The entire mixture was extracted with 10 ml of methanol. All weights were obtained on a Mettler model M5 microbalance.

RESULTS AND DISCUSSION

In a recent paper (14) we have described the use of phenones as internal standards for hplc. The analysis of carbofuran, another carbamate pesticide, was described in this paper. Figure 1 illustrates the separation obtained for the standard propoxur solution. Relative response can be obtained by comparing either peak areas or peak heights for the propoxur and n-butyrophenone peaks when sample weights are known. After obtaining a proper calibration factor from the known standard, one can proceed to analyze unknown samples.

A chromatogram obtained for a 2% commercial rat bait is shown in Figure 2. Data obtained for this sample indicated a confirming assay of 2.05 ± 0.05%. Several runs were obtained to determine this result. Before analysis of the rat bait, a blank run of propoxur free bait was made to check for potential interference. No interference was seen in the area under the n-butyrophenone peak and only low level leading and trailing partially resolved interference was found in the region of the propoxur peak. These low level peaks are not of sufficient magnitude to significantly affect the final result.

From past hplc experience with other pesticide formulation types, such as granules and EC's (emulsifiable concentrates) we speculate

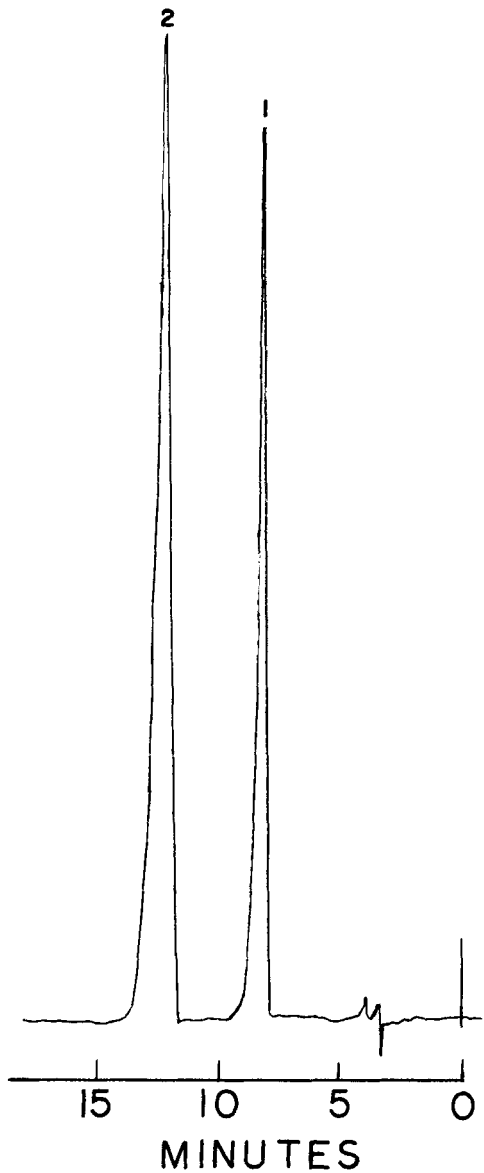

Figure 1. Propoxur Standard Solution (Conditions specified in the text)

1. Propoxur
2. n-butyrophenone

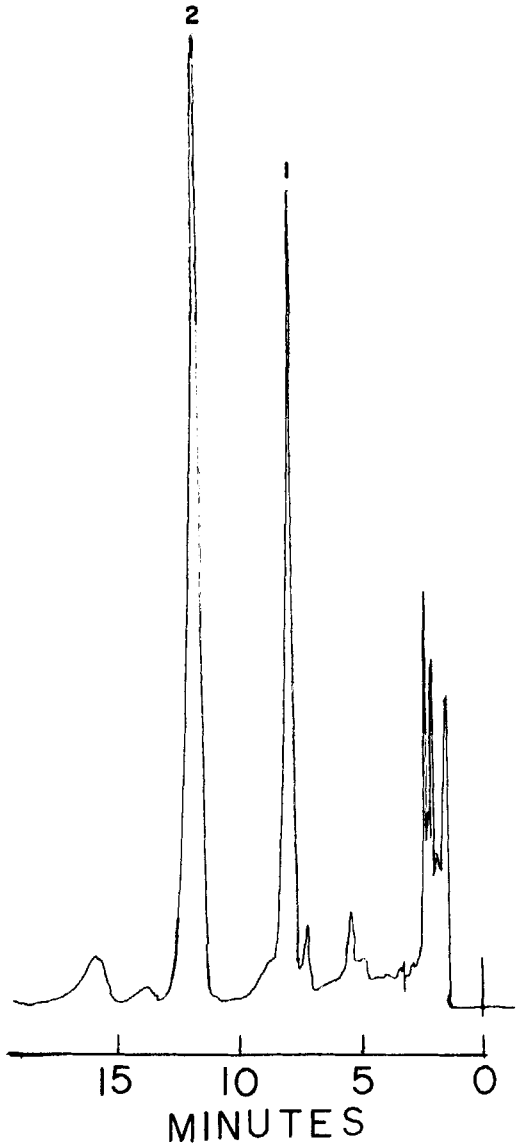

Figure 2. Propoxur 2% Rat Bait (Conditions specified in the text)

1. Propoxur
2. n-butyrophenone

that this method can be easily adapted. EC s normally show early eluting peaks due to the formulation components. These should not interfere with either the propoxur or n-butyrophenone peaks. A note of caution must be mentioned regarding the analysis of EC's. Insoluble or noneluting adsorbed components often tend to collect on the column especially at the inlet. This tendency can significantly decrease column life. If the analysis of EC's is contemplated, the use of a precolumn is suggested. Unfortunately as of this writing, we did not have any EC samples to evaluate. In any event, the rapid elution time and excellent resolution for the technical and rat bait samples established the utility of the method.

CONCLUSION AND SUMMARY

The rapid analysis of propoxur via reversed phase chromatography has been accomplished. The use of n-butyrophenone as an internal standard aids in quantification of results and tends to remove some run to run analytical variability from the work such as the effect of variable injection volumes. Many samples of technical and rat bait have been successfully analyzed utilizing this method.

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