Single Column Gas Liquid Chromatography of Methyl Parathion and Metabolites using Temperature Programming

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The glc separation of a mixture of compounds with a wide range of boiling points can often be accomplished by programmed temperature gas chromatography (ptgc) in which the temperature of the entire column is continuously increased at a uniform rate. Peaks representing low boiling constituents emerge first, essentially as they would from an isothermal column operated at a relatively low temperature. However, the retentions of high-boiling compounds, which on a low-temperature, isothermal column would emerge as delayed flat peaks, will be shortened by the uniformly increasing temperature. Consequently, mixtures of compounds with an extremely wide boiling range may be more rapidly separated with sharper and more symmetrical peaks which are amenable to qualitative and quantitative interpretation.

The column requirements in ptgc are the same as those for isothermal glc. All types of columns may be used since the intrinsic efficiency of the column is independent of the mode of operation (1). However, loss in column efficiency usually occurs due to non-uniform temperature distribution in the column. Since this disadvantage is related to column diameter, small diameter columns (e.g., 4 mm. i.d.) are preferred (2).

The vapor pressures of the liquid phase also increase logarithmically with the temperature, and thus bleeding, resulting in base-line drift, may be a problem. This complication may be avoided by using thermostable phases, dual-column detector compensation, and selective detectors (such as the thermionic detector) which are unresponsive to the bleeding products.

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Although several reports of the separation of pesticide residue using this technique have appeared, to the authors' knowledge this is the first attempt to evaluate the glc of a pesticide and its first-stage metabolites.

Materials and Methods

Materials, methods, and procedures are the same as described previously (3, 4).

Results and Discussion

The dialkyl acid metabolites of methyl parathion cannot be separated from the solvent peak even at 160° C. on an Apiezon L column (Figure 1) under isothermal operation. However, they can be separated from the solvent and resolved into separate peaks with high-loaded columns or by low-temperature glc. Under these conditions, elution of methyl parathion and the other metabolites will be greatly delayed and their peaks will be broad and not amenable to quantitation. The results of ptgc with six of these compounds on a QF-1 column are shown in Figure 2; only methyl paraoxon and desmethyl methyl paraoxon are not resolved, and these are not separated since the latter is converted to the former due to on-column esterification (3).

When ptgc was evaluated for practicability, it was found that relatively few samples could be analyzed per day with meaningful results due to the time necessary for temperature equilibration, and the need for duplicate injections to validate results. Bostwich and Giuffrida (5) also noted this disadvantage and experienced difficulties from bleeding of the liquid phase as well; no bleeding difficulties were encountered in the current study utilizing a thermionic detector. Another significant observation of these authors was that column life is shortened by ptgc and some compounds like azinphosmethyl and coumaphos, which are normally stable, are decomposed or altered. Bowman and Beroza (6) analyzed 20 organophosphorus insecticides including four oxygen analogs on four columns (DC-200, DC-710, QF-1, and DEGS) by ptgc, using a flame photometric detector in both sulfur and phosphorus modes. They did not comment on the reproducibility of their results, which is an important consideration in practical applications. Quantitative variations as large as 10-20

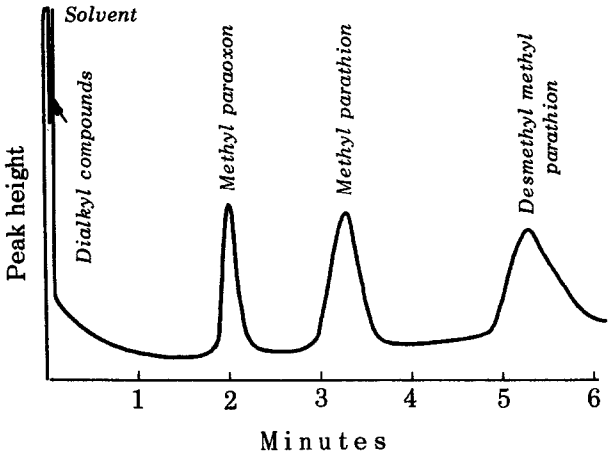

Figure 1. Isothermal separation of methyl parathion and metabolites; column 5% Apiezon L on Gas Chrom Q 80/100, 2'x4 mm i.d.; temperatures of column, flash heater, and detector 160°, 210° and 200° C., respectively; flow rates of nitrogen, hydrogen and air 40, 21, and 300 ml./min., respectively.

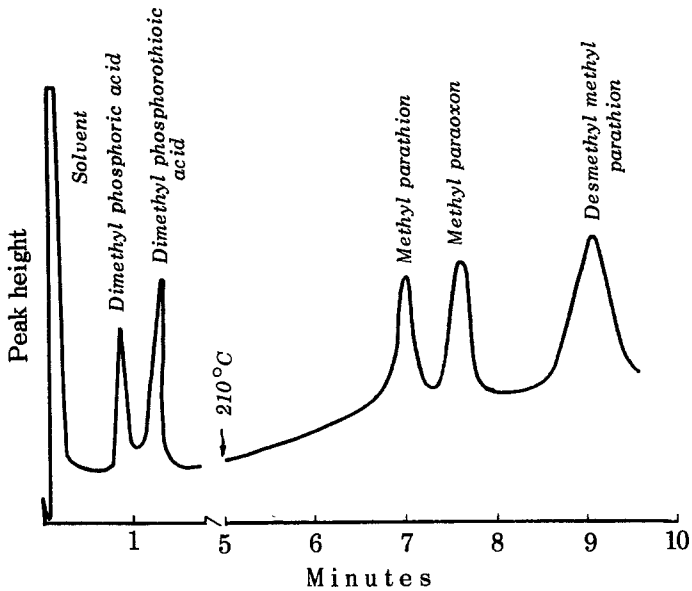

Figure 2. Ptgc separation of methyl parathion and metabolites; column 12% QF-1 on Gas Chrom Q 80/100, 2'x4 mm i.d.; temperatures of flash heater and detector 210° C., column 110° C., ptgc at the rate of 20°/min. to 210° C. (↕) and then isothermal; flow rates of nitrogen, hydrogen and air 40, 21, and 300 ml./min., respectively. Note: chromatogram from 2-5 minutes not shown, no peaks in this interval.

percent were observed in the current study with ptgc, and thus this could be an important limitation. On the other hand, the value of ptgc, in the qualitative separation of compounds of wide volatilities, is evident.

Literature Cited

1. C. Horvath, Practice of Gas Chromatography (L. S. Ettre and A. Zlaekis, Ed., Interscience, New York), p. 129 (1967)

2. K. P. Hupe and E. Bayer, Gas Chromatography (A. Goldup, Ed., The Institute of Petroleum), p. 62 (1965)

3. P. S. Jaglan, R. B. March, and F. A. Gunther, Anal. Chem. In press (1969)

4. P. S. Jaglan and F. A. Gunther, Bull, Environ. Contamin. & Toxicol. In press (1969)

5. D. C. Bostwick and L. Giuffrida, J. Assoc. Official Anal. Chemists 50, 577 (1967)

6. M. C. Bowman and M. Beroza, J. Assoc. Official Anal. Chemists 50, 1228 (1967)