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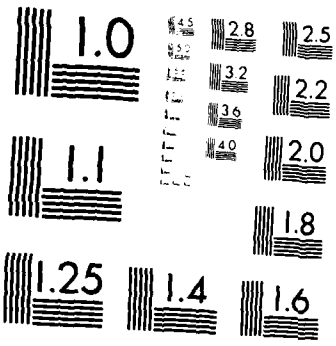

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Dye-assisted, reversed phase, liquid chromatography has been applied to the separation of trace levels of a series of organophasphate compounds. Using dioxane-water mixtures containing 10^{-4}M Brilliant Green as mobile phases and either Partisil-ODS or Lichrosorb-ODS columns. The chromatographic separation of phosphonates, phosphites, and phosphates were accomplished.

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TECHNICAL REPORT NO. 7

"Separation of Organophosphate Compounds by Dye-Assisted Chromatography"

by

T. Gnanasambandan and H. Freiser

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June, 1983

Separation of Organophosphate Compounds

Organophosphates represent a group of compounds that have a wide variety of applications ranging from chemical agents to pesticides that require a simple selective and sensitive trace level analytical technique.

Earlier efforts to develop an analytical method for these compounds utilized the more common chromatographic techniques. Thin layer and liquid chromatography were found to be inadequate because of their lack of sensitivity.(1) GLC with flame photometric detection of phosphorus has been used in the analyses of these compounds but some of these compounds need prior derivatization and most of the compounds cannot be separated with a single column. Ion chromatography(2) offers a sensitive technique for compounds that are phosphoric acids. The esters could be hydrolyzed to the corresponding phosphoric acid for determination. Compounds of similar pKa are found to be difficult to separate, however.

In our last publication(3) we reported a novel HPLC analytical technique for detecting and separating neutrals that are non-chromophoric. The purpose of this report is to show the use of the above technique in the separation of organophosphate compounds and also to establish the chromatographic conditions, that can be used for trace analysis.

Experimental

Materials. The organophosphates used for the study were obtained from various sources and were sometimes purified before

use. Degassed and deionized water, dioxane and methanol were used for all mobile phase preparations. Brilliant Green (Baker Analyzed) was used as received.

Purification of organophosphates. A 1.0ml sample is diluted to 10mL with Analar grade hexane. This solution is twice extracted with 10mL of 1% K_2CO_3. The organic layer is separated and dried over Na_2SO_4 (anhydrous) and 1mL aliquots of the organic phase are diluted with methanol to 10 mL MeOH for analysis. It is necessary to prepare fresh samples to the dilution desired, because the solutionsz do deteriorate within two days.

Apparatus: A modular, high performance liquid chromatograph consisting of an Altex pump (Model 110A), a variable wavelength UV visible detector (Schoeffel Model SF770 Spectraflow), a refractive index detector (Showa Denko KK Shodex RI model SE-11), and a strip chart recorder (Linear Instruments model 261 m/m) was used. Sample injector was 10 uL loop injector (Spectra Physics rotary valve injector).

Mobile phase. The mobile phases used in this study were either dioxane/water or methanol/water. Each mobile phase also contained $1x10^{-4}$M Brilliant Green as the third component.

Columns. Two columns were used in the study. (a) Partisil ODS-2 10u 25cmx0.04cm and (b) Lichrosorb ODS-10u 25cmx0.04cm. Both these columns were slurry packed in our laboratory and had measured efficiencies of about 16,000 plates/meter. The cleaning and determination of the efficiencies of the column are determined as described elsewhere.(3)

Results and Discussion

Several investigators(4) have explored various chromatographic techniques for separating the major organophosphate esters. The present study is different in that we used a dye (Brilliant Green) as a component of the mobile phase to form an 'associate' with the analytes to enhance detection and separation.

Table 1 shows the various organophosphates chosen for our study. Ten compounds were chosen as a representative of the four families--phosphonates, phosphites, phosphate and phosphoramide with a molecular weight range from 113-265.

The first set of experiments were conducted with a Lichrosorb ODS column using a mobile phase containing a mixture of dioxane and water. Dioxane/water mixture was chosen over methanol/water because our earlier studies indicated more efficient separation could be achieved. As we increased the organic modifier, however, dioxane had to be replaced with methanol to avoid creating a high back pressure resulting from the higher viscosity of dioxane.

Table 2 shows the capacity factors obtained for these compounds with various mobile phases. The data shows that good resolution was obtained for these compounds. Using a refractive index detector, we also obtained the capacity factors for these compounds on a dye-free column and using a dye-free mobile phase.

As in our earlier study with alcohols, the use of the dye increased analyte retention, a further indication of dye-analyte interaction.

Figure 1 shows the calibration curve obtained for these compounds. Peak height was plotted as a function of weight of organophosphate. As indicated from the graph, good linearity was obtained in the microgram range.

In separating, tributyl phosphate, dibutyl phosphite and dibutyl butyl phosphonate we had to use 70% methanol/water containing 10^{-4}M Brilliant Green as the mobile phase. Table 3 lists the various capacity factors obtained. As observed earlier and and seen here as well, an increase of organic modifiers in the mobile phase will also result in the decrease of dye held on the column. Usually a negative peak with a characteristic capacity factor was seen after the samples were eluted. Table 3 also indicates that a separation between tributyl phosphate and dibutyl butyl phosphonate is not feasible. Figure 3 shows the calibration curves obtained for these compounds. They show good linearity and could easily be used for analytical purposes.

Although we did not use an extensive number of compounds to study in detail the mechanism of separation we have here clearly established that separation between the organophosphates is feasible and at an order of magnitude better sensitivity than obtained with normal modes of chromatography. Further work is under way.

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1. Crabtree, E. V., and E. W. Sarver, "Review of Analytical Procedures for GB, VX, and their Degradation Products." Edgewood Arsenal Special publication EC-SP-76021, January 1977.

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4. Akoi, Y., M. Takeda, and M. Uchiyama, J. Assoc. Offic. Anal. Chem. 58, 1286, 1975.

Legend for Figures

Figure 1. Separation of Organophosphates.

1.) Diethylphosphite

2.) Hexamethylphosphoramide

3.) Diethylethylphosphonate

Sample size 10uL contains about 80ug.

Experimental conditions: Column Spherisorb ODS 5u 25cm x 4.0mm

Flowrate: 1 mL/min. Detector wavelength: 436nm.

Figure 2. Calibration waves of various organophosphates.

Experimental conditions: Column Lichrosorb 10u ODS 25cm x 4.0mm

Mobile phase Dioxane/water 10:90 V/V% with 10^{-4}M Brilliant Green. Flow role 1 mL/min. detection wavelength 436nm.

Figure 3. Calibration curve of various organophophosphate.

Experimental conditions: Column Partisil ODS-2-10uM (25cmx0.04)

Mobile phase 75:25 V/V% MeoH/H_2O with 10^{-4}M Brilliant Green. Flow rate 1 mL/min. detection at 620nm

Table 1

Capacity Factors of Organophosphates (I)

MOBILE PHASE		30% MeOH/H_2O V/V WITH 10^{-4} M BG	10% DIOXANE/H_2O WITH 10^{-4} M BG
	ANALYTE	k'	k'
(DMMP)	Dimethylmethyl phosphonate	.6	.8
(DEEP)	Diethylethyl Phosphonate	4.4	6.9
(HMNP)	Hexamethyl Phosphoramide	3.1	3.5
(DEP)	Diethyl Phosphite	1.6	2.5
	Phosdrin (methyl 3-hydroxy and crotonate, dimethyl phosphate)	6.3	ND
(DDVP)	Dichlorvos (2,2,-dichlorovinyl dimethyl phosphate)	2.8	ND

Column Partisil ODS-2 10um (25cm x 4.0mm id)

Flowrate 1nl per min.

Detector visible 436

Table 2

Capacity of Factors of Organophosphates (II)

MOBILE PHASE 75% MeOH/H_2o V/V WITH 10^{-4} B.GREEN

	ANALYTE	k'
(DBP)	Dibutyl Phosphite	1.3
(DBBP)	Dibutylbutyl Phosphonate	3.2
(TBP)	Tributyl Phosphate	3.2
(TTP)	Tritolyl Phosphate	5.6

Column Partisil ODS-2 10u (25cm x 4.0mm id)

Flowrate 1 mL/min.

Detector wavelength 625nm.

Figure 1

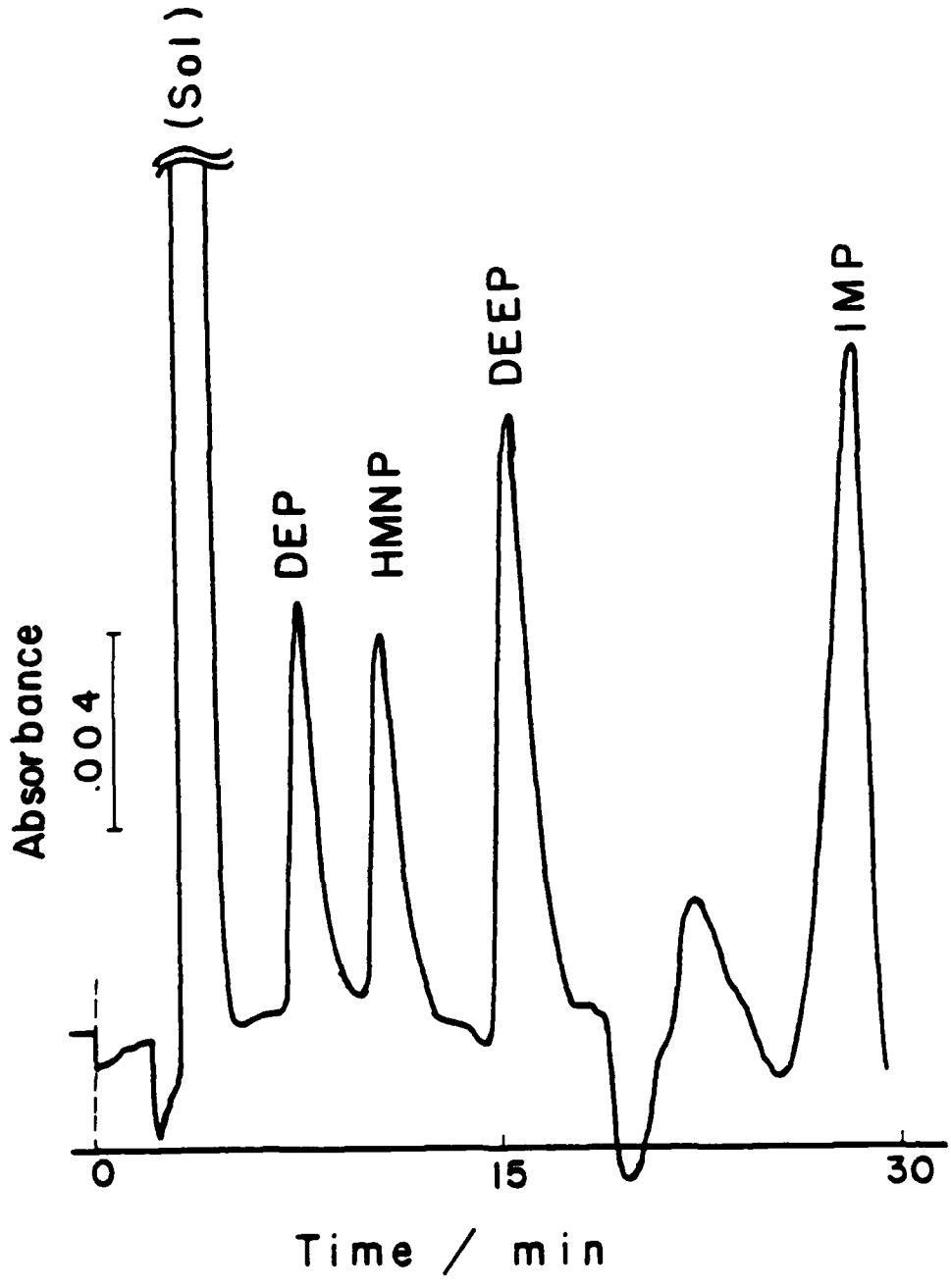


Figure 2

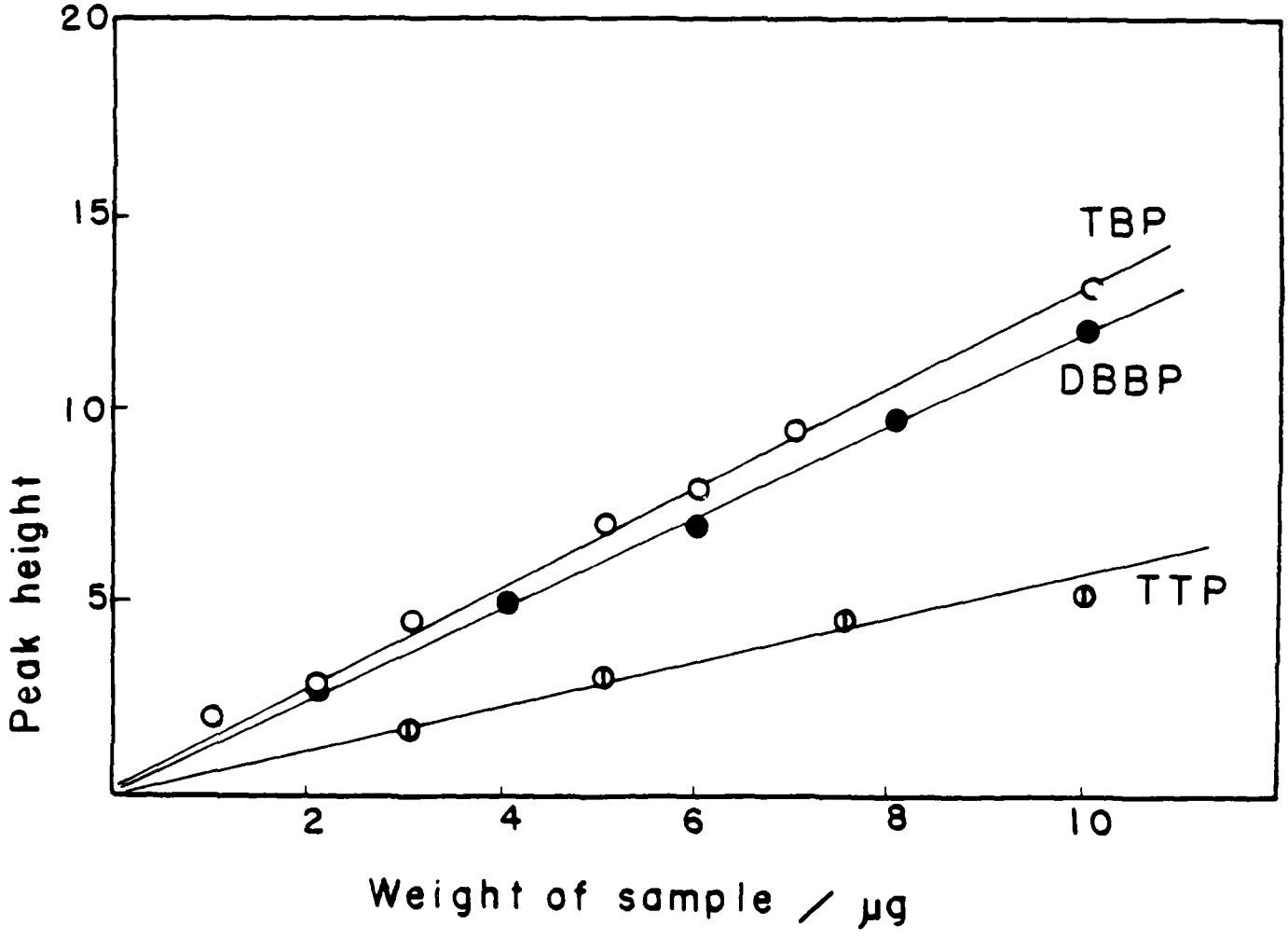
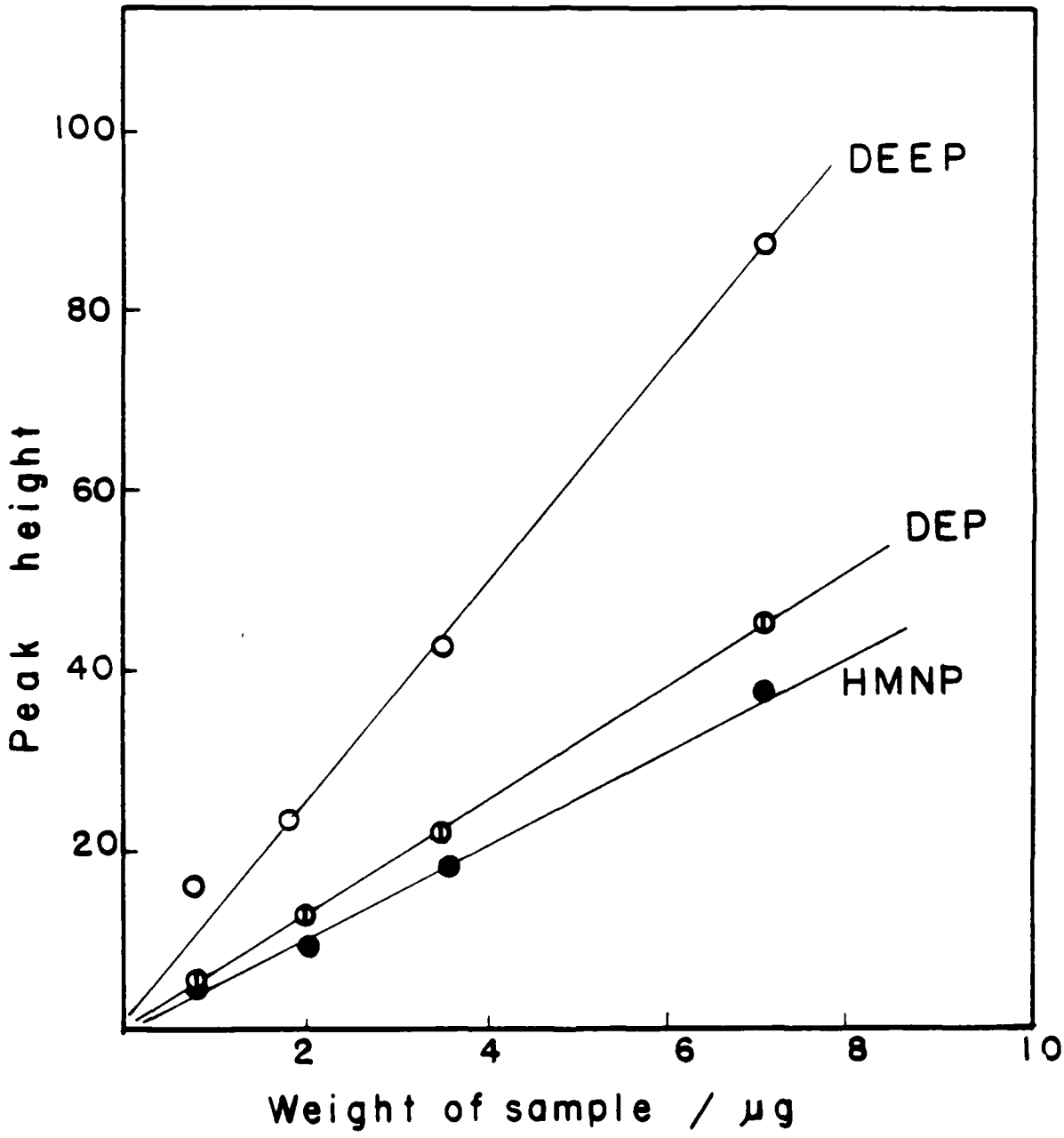


Figure 3


100
80
60
40
20
Peak height
DEEP
DEP
HMNP
2
4
6
8
10
Weight of sample / µg

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