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Note

Support material effects in gas chromatographic analyses of organophosphorus compounds

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Organophosphorus compounds with the general formula $(R_1O)(R_2)(X)PY$, where R_1 = alkyl, R_2 = alkyl or alkoxy and $Y = O$ or S , are often used as pesticides and some are potential warfare agents. They can be divided into two groups: if X is a halogen or cyanide group, the compound is rather volatile and can be analyzed by gas chromatography (GC) without difficulty; X can also represent dialkylaminoalkylthio, amidoalkylthio or nitrophenylthio groups, and these compounds have much lower vapour pressures. Most of these compounds are unstable at higher temperatures (pyrolysis of some of them begins at 150°) and it is necessary to use low-loaded, non-polar columns in order to obtain reasonable retention times. The possibilities of reactions between the solute and the column support material is consequently increased. Thus, if the support material used is not inert¹, it is very difficult to analyze small amounts of polar compounds.

Jaglan and co-workers^{2,3} suggested the use of Gas-Chrom Q and Teflon as the support material for analyses of parathion and its metabolites. Conder⁴, however, showed that Teflon is not an inert GC support. Bevenue and coworkers⁵ found that Chromosorb G, Gas-Chrom Q and Chromosorb W-HP were suitable as support materials for the analysis of mixtures of methyl parathion, ethyl parathion, ethyl paraoxon, malathion and malaoxon. Ives and Giuffrida⁶ improved non-polar columns for analyses of organophosphorus pesticides by adding a polar phase. Other "tail reducers" in GC were reviewed by Ottenstein⁷.

In this work, a comparison has been made between some solvent-support combinations for three model substances.

EXPERIMENTAL

Substances analyzed

As model substances, O-ethyl S-2-(N,N-diisopropylamino)ethylmethylphosphonothioate (DEMO), parathion and dimethoate were used.

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Support materials

Columns were prepared from commercially available support materials such as Chromosorb W HP, Chromosorb G AW DMCS, Gas-Chrom Q, Haloport F and Corning GLC 110 textured glass beads, all 80–100 mesh and used without further treatment.

Liquid phases

OV-1 and OV-101 were applied on to the diatomaceous earths by the infiltration technique⁸. Teflon and glass beads were coated by rotary evaporation. A 1% coating was used in all instances.

Gas chromatographic conditions

All analyses were performed with an F & M Model 400 gas chromatograph equipped with a flame ionization detector (FID). The U-shaped glass columns (1.5 m × 2.0 mm I.D.) were pre-washed with methanolic potassium hydroxide solution, water, acetone and toluene, followed by silanization with dimethyldichlorosilane in toluene and a final wash with toluene and acetone. The newly prepared columns were conditioned at 250° overnight before use. The column temperature was set so as to give the same difference in retention time between *n*-pentadecane and *n*-eicosane on each of the columns used; this corresponded to temperatures between 140 and 150°. The temperature of the injection block was kept at the column temperature and that of the detector was 200°. Injections were made directly into the column. The carrier gas (nitrogen) flow-rate was 20 ml/min. A digital integrator (HP Model 3370A) was used for the quantitative measurements. In some experiments, the integrator was used in the logarithmic output signal mode in order to permit a direct comparison of the peak shapes over a wide concentration range.

RESULTS AND DISCUSSION

Fig. 1 shows chromatograms of various amounts of DEMO, dimethoate and parathion obtained on a column with 1% OV-101 on Gas-Chrom Q. DEMO and dimethoate gave abnormal, prolonged retentions (*i.e.*, retention time measured to the peak maximum) at smaller amounts. The severe tailing of the peaks indicates strong adsorption to the support materials, as can be expected for a polar solute on a low-loaded, non-polar stationary phase¹. The prolonged retention with decreasing amount of substance may be an indication of a convex adsorption isotherm for the support. Common means of saturating active sites, such as injection of large amounts of the compound itself or of silylating agents, did not improve the results. Parathion had a constant retention over the concentration range studied but still exhibited tailing.

Similar results were achieved with the Chromosorb G columns. Chromosorb W HP as the support material seemed to be the least adsorptive diatomaceous earth, but the retention was still a function of the amount injected (6.5 and 3 min for 0.1 and 1 µg of DEMO, respectively). An attempt to deactivate this support was made, but pre-impregnation with about 0.5% (w/w) Carbowax 20M did not improve the results.

In spite of the difficulties involved in preparing columns of the Teflon support

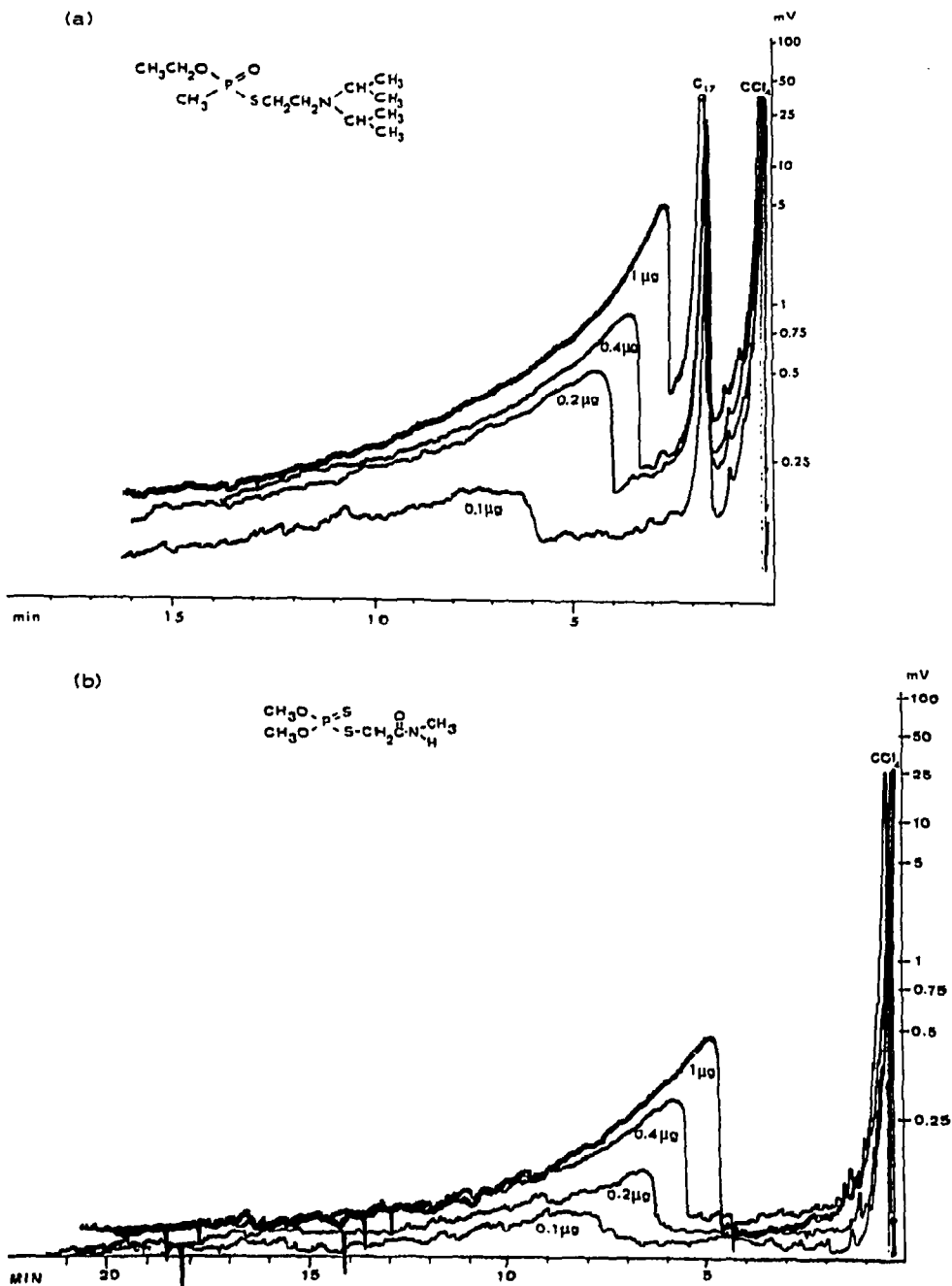


Fig. 1.

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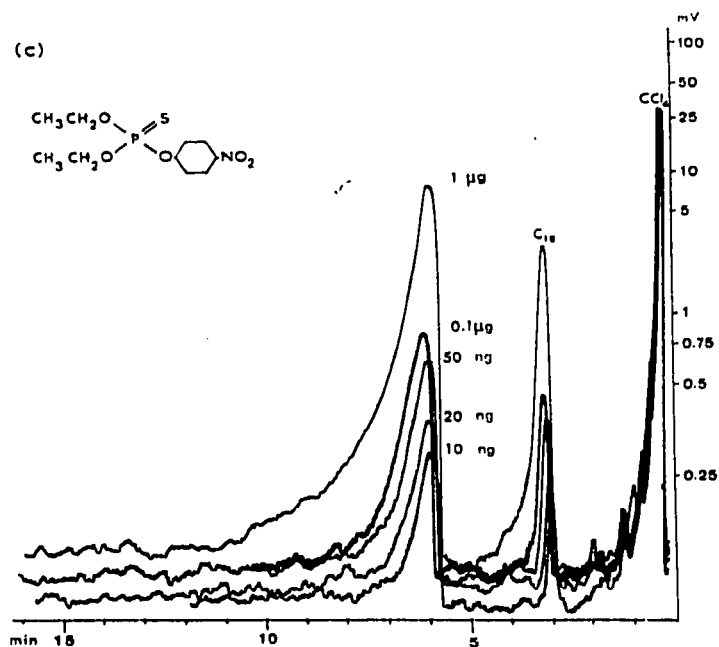


Fig. 1. Chromatograms on Gas-Chrom Q with 1% OV-1; 0.1–1 μg of (a) DEMO, (b) dimethoate and (c) parathion. Sample size: 1 μl . The integrator is in the logarithmic output signal mode in order to permit a direct comparison of the peak shape within the concentration range.

material, these turned out to be useful for parathion and dimethoate. However, as the adsorption of DEMO was very strong, it could not be detected even when microgram amounts were injected into these columns.

Columns with the textured glass beads gave well shaped peaks for all substances investigated, even at the lowest concentrations detectable with the FID. The retention also seemed to be constant and thus independent of the amount injected. Fig. 2 shows the chromatograms for various amounts of DEMO, dimethoate and parathion analyzed on a column with 1% OV-101 on Corning GLC 110. It should be noted that the impurity in DEMO, shown in Fig. 2a, cannot be detected in the chromatogram in Fig. 1a. The impurity is either masked by the severe tailing or the substance is of the same type as DEMO and could be expected to behave in a similar manner, *i.e.*, the retention is a function of the amount injected.

A comparison of the columns studied is shown in Fig. 3. The relative retention times for DEMO are plotted against the amounts analyzed. It is obvious that columns with OV-1 as the stationary phase on diatomaceous supports are inferior to those with OV-101. This may be explained by a higher molecular diffusion of the solute molecule into the more viscous OV-1 and hence there is a greater possibility for interactions with the support material. Such differences in molecular diffusion have been observed⁹ for the two silicone phases SE-30 and SF-96, which are similar to OV-1 and OV-101, respectively.

The columns investigated gave HETP values for *n*-pentadecane and *n*-eicosane in the order Gas-Chrom Q < Chromosorb W HP < Chromosorb G < GLC 110 <

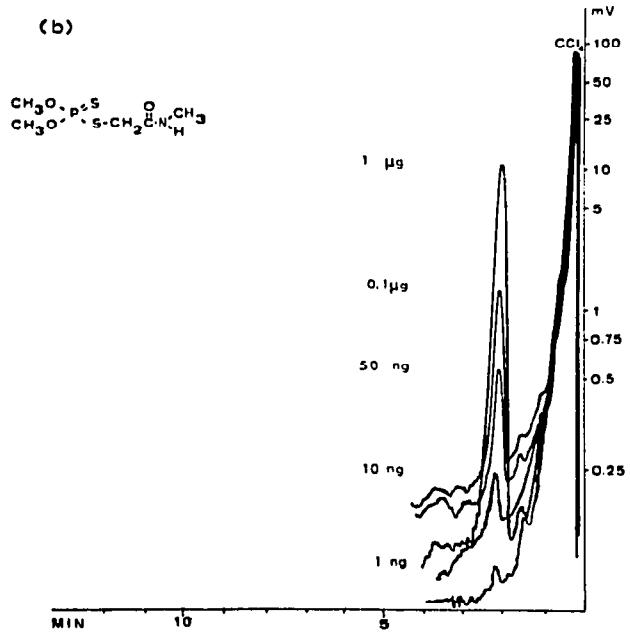
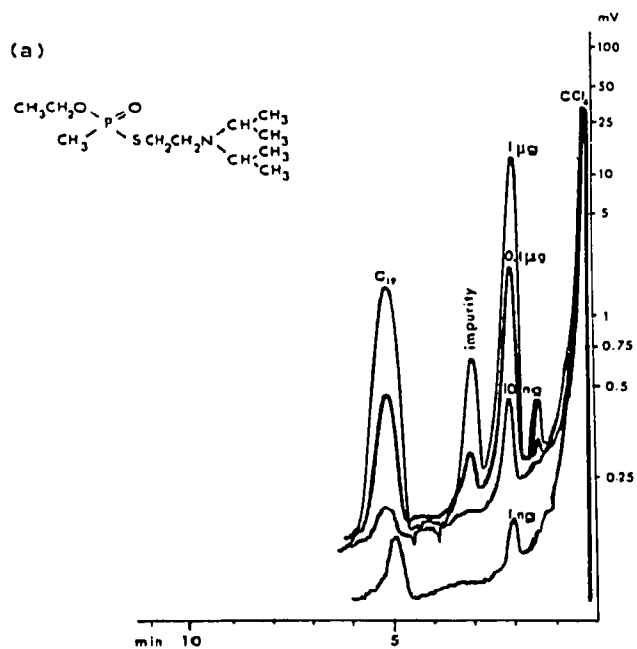


Fig. 2.

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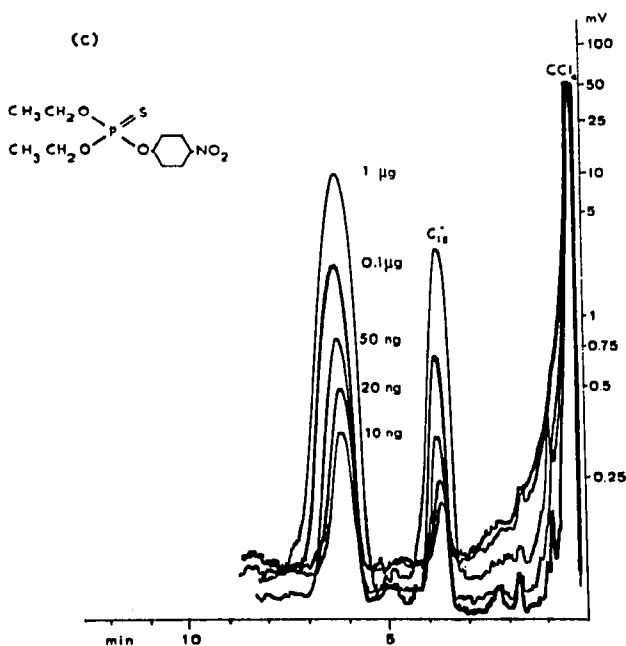


Fig. 2. Chromatograms on GLC 110 glass beads with 1% OV-101; 1 ng-1 μ g of (a) DEMO, (b) di-methoate and (c) parathion. Sample size: 1 μ l. The integrator is in the logarithmic output signal mode in order to permit a direct comparison of the peak shape within the concentration range.

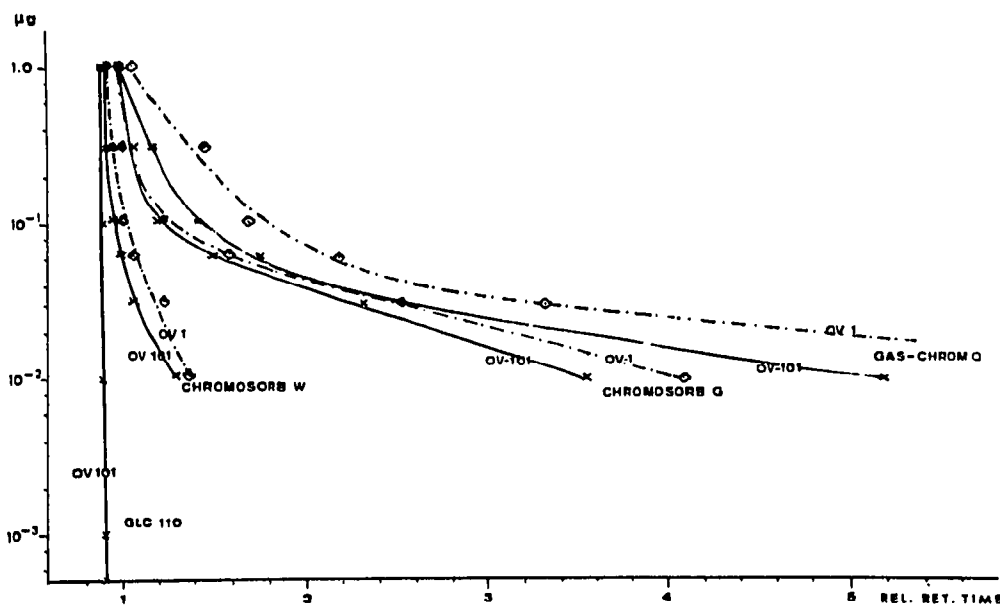


Fig. 3. Solute concentration as a function of relative retention time for analyses of DEMO on Gas-Chrom Q, Chromosorb G, Chromosorb W HP and Corning GLC 110 glass beads. Continuous lines represent OV-101 and broken lines represent OV-1 as the stationary phase.

Teflon, and no marked difference between OV-1 and OV-101 as the stationary phases. For the phosphorus compounds studied, OV-101 gave a lower HETP than OV-1 on each support material. Most striking are the poor results for Gas-Chrom Q columns, as this support material is normally regarded as suitable for use with polar compounds.

CONCLUSIONS

Columns with silanized textured glass beads as the support material and a methyl silicone oil, such as OV-101, as the stationary phase, are preferable for GC analyses of thermally unstable, low volatile, polar phosphorus compounds. The advantages they offer are sharp peaks with little or no tailing, constant retention over a wide concentration range, no loss of solute due to adsorption and the possibility of analyses at the nanogram level.

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