THE SEPARATION OF ORGANOPHOSPHATE PESTICIDES USING BPX90

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Introduction and Discussion

This study examines the retention of organophosphoate and phosphothioate pesticides (OPs) by gas chromatography-mass spectrometry (GCMS) using a BPX90 capillary column (Table 1). Chromatographic characteristics are compared with retention on a non-polar column (BPX5) under identical conditions.

The isothermal elution of OPs from BPX5 and BPX90 columns shows no significant correlation (Fig1). Notable changes in retention character are observed for dioxathion and OPs carrying a substituent with an extended π-electron system. Retention by BPX5 shows a strong correlation with molecular weight (Fig 2). Barriers to forming a continuous π-surface about the oxygen dihedral bridge (planar) divides the OP population with planar analytes eluted earlier than those of similar molecular weight that are out of plane about the bridge.

The same influence on retention is not observed for BPX90. The shift in OP retention between BPX5 and BPX90 shows structure dependent correlation with the octanol-water partition coefficient (K_{ow}) (Fig 3). K_{ow} is a useful measure of partitioning as it gauges the surface chemistry of the analyte by measuring interactions in a polar environment. The correlation is linear for planar and out of plane conformed OPs. The out of plane group is further divided with unsaturated and aromatic OPs showing different shifts in retention to those OPs having aliphatic substituents. Rotation of each series away from the vertical (i.e. no difference between phases) to horizontal (i.e. orthogonal retention that is independent of K_{ow}) is a measure of phase orthogonality.

aspon	dicrotophos	isomalathion	pyridaphenthion
butamifos	dimethoate	isoprothiolane	Ronnel
chlorfenvinfos (cis)	dioxathion	isoxaoxon	sulfotepp
chlorfenvinfos (trans)	disulfoton	isoxathion	sulphrofos
chlorpyrifos ethyl	EPN	leptophos	TEPP
chlorpyrifos methyl	ethion	malaoxon	terbufos
coumaphos	ethoprop	malathion	tetrachlorvinphos
cyodrin (crotoxyphos)	famphur	merphos	thionazin
DEF(oxymerphos)	fenitrothion	mevinfos	tokuthion
demeton-O	fenitroxon	monocrotophos	tolclofos methyl
demeton-S	fensulfothion	parathion ethyl	trichloronate
diazinon	fenthion	parathion methyl	trimethyl phosphothioate
dichlofenthion	fonofos	phorate	trithion
dichlorvos	isofenphos	phosphamidone	

Table 1: OP compounds included in the study.

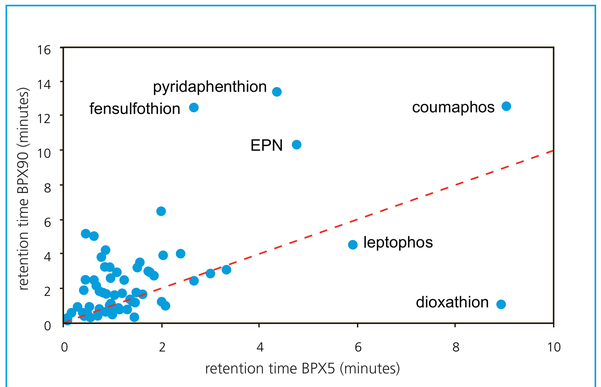


Figure 1: A scatter plot of OP retention times for BPX5 versus BPX90 with some outliers labelled. Retention times are corrected for the solvent peak. (Experimental conditions: Injector 275 °C, injection volume 0.1 µL at 60:1 split. Oven 100 °C, flow rate 1.2 mL/min. MS 40-500 Da at 2 scan/sec.)

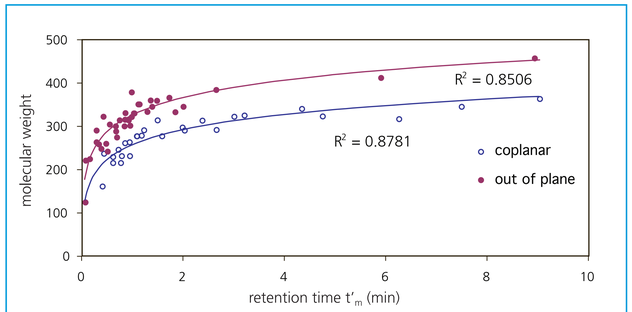


Figure 2: BPX5 retention time for OPs versus molecular weight. The population is divided on the basis of functionality (steric effects and through conjugation).

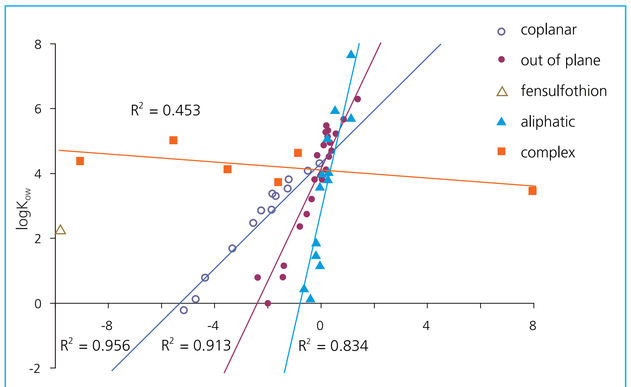


Figure 3: Difference in isothermal retention time between BPX5 and BPX90 columns operated under identical conditions (tr'(BPX5)-tr'(BPX90)) versus log K_{ow}. The population is divided on the basis of functionality (steric volumes and through conjugation).

Discussion (continued)

Correlation with K_{ow} is weaker for OPs with substituents having an extended π-system; as the substituent dominates the retentive mechanism. Dioxathion also fits this series because it shows the same dominance of substituent group over P=S interaction with the phase. Fensulfothion is an outlier to all types and shows retention somewhere between planar and complex.

Conclusion

Retention on a BPX90 column is determined by steric access to the π –electron structure, the presence of hard or soft double bonds (e.g. phosphoates and phosphothioates), planarity, free rotation and lipophilicity. In contrast, non-polar retention shows a clear association between molecular weight which, under isothermal conditions, is attributable to both conventional Henry's Law behavior and to analyte mobility.

Non-polar retention of OPs may be sub-divided on the basis of intramolecular mobility (free rotational barriers and the possibility of through conjugation). In contrast, retention of the same target group by BPX90 is complex and influenced by functionality rather than molecular size. The correlation of retention differences between the phases with octanol-water partition coefficient reflects the influence of surface chemistry (steric and lipophilic factors) on the ability of BPX90 to interact with analytes.

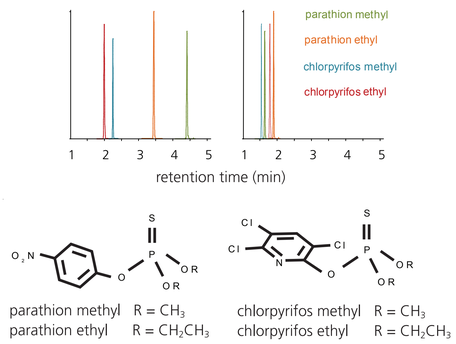
The specific interactions of the BPX90 phase make it highly orthogonal to the non-polar phases and so it is suitable for not only primary separation of some analytes but also a suitable choice as a second column in multidimensional techniques.

SPECIATION OF METHYL AND ETHYL ORGANOPHOSPHATES

On non-polar phases, OP methyl esters are eluted before the analogous ethyl esters. Increasing the molecular weight and steric volume of the non-polar substituents reduces the analyte vapor pressure, decreases mobility which increases retention on a BPX5 column.

When the same analogous pairs of dimethyl and diethyl OPs are chromatographed on a BPX90 column, the elution order is reversed relative to elution from a non-polar phase (Fig 4). While the third substituent of each OP contributes significantly to spatial configuration, the chain length of the alkyl moiety determines steric access of the GC phase's cyano groups to the phosphoate or phosphothioate moiety. Reduced interaction with the underlying electron sump of the phosphoate or thioate leads to earlier elution. The limited free rotational reach of the O-methyl groups makes their steric interference significantly weaker than the corresponding ethyl analogues and thus the methyl esters are more strongly retained than their higher homologues.

The elution order reversal observed for dimethyl and diethyl ester pairs is useful in structural elucidation, achieving alternative resolution outcomes and as a compliment to non-polar phases for multi-dimensional approaches to analysis.



parathion methyl R = CH_3
parathion ethyl R = CH_2CH_3
chlorpyrifos methyl R = CH_3
chlorpyrifos ethyl R = CH_2CH_3

Figure 4: The isothermal separation of methyl and ethyl analogues of the phosphothioates chlorpyrifos and parathion on BPX90 (left) and BPX5 (right) columns.

Columns 30 m x 0.25 mm i.d., 0.25 µM film thickness. Injector temperature 275 °C, oven 50 °C (1min) then 15 °C/min to 260 °C (10 min). Injection splitless 1 µL in acetone. Carrier gas helium at 1.2 mL/min constant flowrate. MS acquisition from 40-500 Da at 2 scan/sec.

SPECIATION OF PHOSPHOTHIOATES AND THEIR OXON ANALOGUES

In contrast to non-polar phases, elution of oxon and thion OP analogues is reversed on a BPX90 column (Fig 5). The stronger retention of the oxons is attributable to the relative electonegativities of oxygen and sulphur that make the phosphorous – oxygen double bond harder than the phosphorous – sulphur double bond with its larger n-electron shielded sulphur atom. These retention characteristics suggest that BPX90 selectivity is directed towards individual bonds on the basis of their 'hardness' or π-density.

When coupled with a large aromatic substituent (e.g. isoxathion and isoxaoxon), elution order reversal is also coupled with increased retention times that are attributable to the higher affinity of the BPX90 for compounds with a high aggregate unsaturation.

The elution order reversal is potentially useful for elucidation of structure, achieving alternative resolution outcomes and as a compliment to non-polar phases for multi-dimensional approaches to analysis.

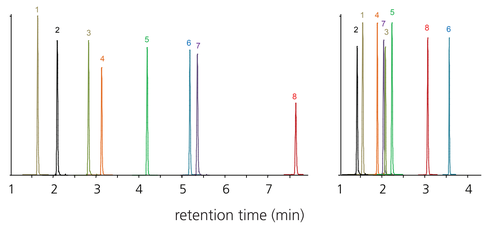
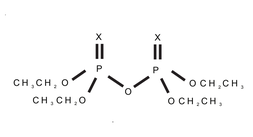
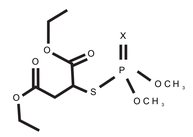


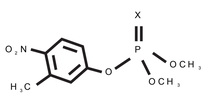
Figure 5: The isothermal separation of phosphosthioate and phosphoate (or oxon) analogues of OP pesticides on BPX90 (left) and BPX5 (right) columns. Compounds are sulfotepp (1), TEPP (2), malathion (3), malaoxon (4), fenitrothion (5), isoxathion (6), fenitroxon (7) and isoxaoxon (8). (Experimental conditions as for Fig. 2)



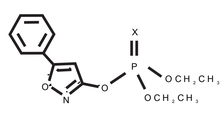
(1) sulfotepp X = S
(2) TEPP X = O



(3) malathion X = S
(4) malaoxon X = O



(5) fenitrothion X = S
(7) fenitroxon X = O



(6) isoxathion X = S
(8) isoxaoxon X = O

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