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STRUCTURE-RESPONSE RELATIONSHIP OF GAS CHROMATOGRAPHY-FLAME PHOTOMETRIC DETECTION TO SOME ORGANOPHOSPHORUS COMPOUNDS

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SUMMARY

A variety of organophosphorus compounds was studied with respect to their response to the gas chromatographic-flame photometric detector. Contrary to the experience of some investigators, the molar response of phosphorus was found to be linear only within homologous series. Compounds containing the dialkylaminoalkyl moiety on phosphorus are in the low sensitivity (50% of the "normal" molar sensitivity) range. Some compounds such as phosphodihalides (fluoro or chloro) are 30% or more above the "norm". Comparative data are given for selected compounds on the flame ionization and thermionic nitrogen-phosphorus detectors. A postulated mechanism is given for explaining some of the differences.

INTRODUCTION

The investigation described here was initiated to explain differences observed in the relative gas chromatographic (GC)-flame photometric detector (FPD) sensitivity among a variety of organophosphorus compounds. During the course of GC analytical development in our laboratory from 1968 to 1972 it had been observed that certain of the organophosphonate compounds did not give predictable molar FPD sensitivities. With some functionalities the sensitivities were even 50% or less than those expected.

The application of the FPD was first reported by Brody and Chaney¹ based on the patent of Draeger and Draeger² and was designed to detect the flame emission from phosphorus (526 nm) attributable to HPO, and from sulfur (394 nm) as S₂. These investigators and others³⁻⁵ demonstrated that the photometric response of their phosphorus detector was linear with respect to concentration. On extrapolation of this information to variation in percent phosphorus, the intimation would be that sensitivity should be directly proportional to molar concentration.

The experimental results described here represent our attempt to determine which variables might be responsible for the observed difference in FPD phosphorus

sensitivity among a variety of organophosphate and phosphonate compounds. Included in this study was the comparative application of the more recently available thermionic nitrogen-phosphorus detector (NPD) in the phosphorus mode.

EXPERIMENTAL

The experimental design of the investigation was predicated on the premise that (a) the amplitude at the wavelength maximum of 526 nm might vary with the nature of the groups on the phosphorus atom, *i.e.*, P-N, P-O-C-C-N, P-CH₃, P-F, etc., (b) that the efficiency of burning might depend on the substituents on the P atom, (c) that certain substituents such as halogens might enhance the sensitivity additively, (d) that ionic interferences positive or negative might be existent⁶ or (e) that certain of the compounds might have shown more efficient migration through the columns.

All of the compounds were to be diluted in the same solvents and the molar responses determined. Most of the determinations would be made using a QF-1 column. Substrates of lower polarity such as SE-30 and OV-17 would be used on selected compounds to preclude overlooking potential column effect on the molar response of FPD. In addition, both the flame ionization detector (FID) response and effect of retention time or retention index would be considered. Correction would be made where necessary to eliminate purity of sample or the nature of impurities as a variable.

Determinations would be made, where possible, employing flame emission measurement. For practical purposes this would be a means for ascertaining the emission wavelength maxima and relative sensitivity independent of GC. For this study an available atomic absorption, flame emission spectrophotometer was to be employed.

Procedures

The GC work described in this report was performed on Perkin-Elmer Model 900 and 990 gas chromatographs equipped with FID, NPD, and FPD detectors with a Hewlett-Packard Model 3380A report integrator. Flame emission spectra were obtained on a Perkin-Elmer Model 460 atomic absorption, flame emission spectrometer with hydrogen as the fuel and argon as the diluent gas. The chromatographic conditions employed and column parameters were as follows. The FPD coupled to Model 990 was operated with a 526 nm interference filter. The electrometer range was 10² (as needed), the attenuation range $\times 256$ (as needed) and the nitrogen carrier gas set at a flow-rate of 75 ml/min. The fuel gases were hydrogen at 150 ml/min; oxygen at 20 ml/min; and air at 20 ml/min. The detector temperature was at 160°, the injection port at 200° and the manifold at 250°. The basic system for all of the compounds was a 182.9 cm \times 2.0 mm I.D. Pyrex glass column containing 10% QF-1 on 80-100 mesh Gas-Chrom Q. The column temperature was programmed from 60°-200° C at 8°/min.

The other columns employed were of 182.9 cm \times 2.0 mm I.D. Pyrex glass containing 20% SE-30 on 60-80 mesh Gas-Chrom P and 3% OV-17 on 80-100 mesh Gas-Chrom Q. The FID was operated on the Perkin-Elmer Model 900 at 250° with a fuel feed of hydrogen at 50 ml/min and air at 350 ml/min. The electrometer was set

at 10 (as needed) and the attenuation at 2 (or as needed). The NPD coupled to the same chromatograph was operated in the phosphorus mode with helium at 40 ml/min, hydrogen at 50 ml/min and air at 200 ml/min. The electrometer range was 10 (as needed) and the attenuation $\times 8$ (as needed). The detector temperature was maintained at 250° while other column conditions were identical to those of the FPD.

The sample concentrations employed ranged from 1 to 200 ng/ μ l with sample injections from 1–8 μ l depending on the detector.

Diisopropyl methylphosphonate (DIMP) was used as a reference to be compared against other structural responses. A calibration curve was prepared using DIMP as a standard to measure the relative responses of the phosphorus compounds and to allow close correction for day-to-day instrument variables. This curve was consistently linear with respect to concentration *versus* integrated area. A correction factor could be applied to all compounds studied on a particular day. In this manner, compensation could be made for any daily column or detector variable. The response level for each compound was determined from the integrated area of the chromatogram divided by the concentration of the sample injected into the instrument, and then the levels of response were averaged to give a common response for the compound being analyzed. The calculations used to obtain molar response follow:

$$\text{Weight percent P} = \frac{30.98 \times 100}{\text{Molecular weight of compound}}$$

$$\text{Relative response} = \frac{\text{Integrated area}}{\text{Concentration of sample injected}}$$

$$\text{Molar response} = \frac{\text{Relative response}}{\text{Weight percent P}}$$

RESULTS AND DISCUSSION

A variety of organophosphorus compounds were chromatographed employing the FPD in the phosphorus mode, and a few selected compounds detected by the NPD also in the phosphorus mode. Purities of the test compounds had been determined, where applicable, by the hydrolytic method for G agents⁷ and the thioate procedure as for VX and related compounds⁸ and by GC employing thermal conductivity (TCD) directly⁹ and with internal standard such as via retention indices. The phosphoramidohalide compounds such as Tabun were assayed by a combination of hydrolytic and fluorine¹⁰ or chlorine determinations, as well as by GC.

In all cases the compounds showed purities of at least 85% with most above 90%. For purposes of the study all calculated molar responses were corrected for the determined purities and potentially deleterious impurities.

The organophosphorus compounds investigated included alkyl phosphate and alkylphosphonate esters (DIMP, etc.), methylphosphonahalides (Sarin type compounds and intermediates), dimethylaminophosphoramidates (Tabun, amidophosphorohalides, etc.), dialkylaminoalkyl methylphosphonate types and others, halo and dialkyl morpholinophosphoramidates (DMMPA and related compounds), *p*-nitrophenyl phosphates (parathion and paraoxon) and some in the miscellaneous category.

TABLE I
MOLAR RESPONSE FOR SOME ORGANOPHOSPHONATE AND PHOSPHATE ESTERS, EMPLOYING THE FLAME PHOTOMETRIC DETECTOR

Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	DMMP	Dimethyl methylphosphonate	124	23.00	20.5
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	DMMPS	Dimethyl methylphosphonothionate	140	23.14	20.2
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	TMPO	Trimethyl phosphate	140	23.14	19.9
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \end{array}$	DEMP	Diethyl methylphosphonate	152	20.39	19.6
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-SCH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \end{array}$	S-M,O-EMP	S-Methyl,O-ethyl methylphosphorothionate	154	20.13	20.0
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{-P-OCH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \end{array}$	DEEP	Diethyl ethylphosphonate	166	18.67	20.1
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_2\text{CH}_3 \\ \\ \text{OCH}_3 \end{array}$	EMMP	Ethyl methyl methylphosphonate	138	22.66	20.7

$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OCH}(\text{CH}_3)_2 \\ \\ \text{OCH}_3 \\ \text{S} \end{array}$	Isopropyl methyl methylphosphonate	152	20.40	20.9
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-(OCH}_2\text{CH}_3)_2 \\ \\ \text{O} \end{array}$	Diethyl methylphosphonothioate	168	18.45	20.0
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-SCH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$	O-Ethyl S-ethyl methylphosphonothioate	168	18.45	20.0
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OCH}(\text{CH}_3)_2 \\ \\ \text{OCH}(\text{CH}_3)_2 \\ \\ \text{O} \end{array}$	Diisopropyl methylphosphonate	180	17.22	18.9
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OC}(\text{CH}_3)_2 \\ \\ \text{H} \\ \\ \text{CH}_3 \end{array}$	Dipinacolyl methylphosphonate	264	11.73	20.2
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{O-P-OCH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$	Tri- <i>n</i> -propyl phosphate	224	13.84	20.6
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O-P-OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$	Tri- <i>n</i> -butyl phosphate	266	11.62	19.4
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{-O-P-O-C}_6\text{H}_5 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Triphenyl phosphate	326	9.51	23.5

TABLE II
MOLAR RESPONSE FOR SOME DIMETHYLAMINOPHOSPHORAMIDATE COMPOUNDS EMPLOYING FPD

Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{CH}_3 \\ \\ \text{F} \\ \text{O} \end{array}$	DMAMPF	N,N-Dimethylamino methyl-phosphoramidic fluoride	125	24.80	22.1
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{F} \\ \\ \text{F} \\ \text{O} \end{array}$	DMAPPZ	N,N-dimethylphosphoramidic difluoride	129	24.03	39.4
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{OCH}_2\text{CH}_3 \\ \\ \text{C}\equiv\text{N} \\ \text{O} \end{array}$	Tabun	Ethyl N,N-dimethylphosphoramidocyanidate	162	19.13	17.1
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{N}(\text{CH}_3)_2 \\ \\ \text{N}(\text{CH}_3)_2 \\ \text{O} \end{array}$	HMPA	Hexamethylphosphoramide	179	17.32	22.2
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{OCH}_2\text{CH}_2\text{Cl} \\ \\ \text{C}\equiv\text{N} \\ \text{O} \end{array}$	Chlorotabun	2-Chloroethyl N,N-dimethyl-phosphoramidocyanidate	196	15.81	22.9
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{OCH}_2\text{CH}_2\text{Cl} \\ \\ \text{F} \\ \text{O} \end{array}$	CEDMAPF	2-Chloroethyl N,N-dimethyl-phosphoramidofluoridate	189	16.40	23.9
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}-\text{OCH}_2\text{CH}_2\text{OCH}_3 \\ \\ \text{F} \\ \text{O} \end{array}$	MEDMAPF	2-Methoxyethyl N,N-dimethyl-phosphoramidofluoridate	185	16.76	23.6

The organophosphorus compounds shown here are examples of at least 50 of those studied and are sufficient to give some indication of structure *versus* FPD molar sensitivity criteria.

The compounds as selected were compiled initially on the basis of their homologous or analogous relationship and their respective molar responses found via GC using the FPD. The GC results for the organophosphonate and phosphate esters are shown in Table I.

From Table I it is quite apparent that little difference in molar response is observed despite the variety of substituents on the phosphorus atom. The molar response is in the 19.6 to 20.6 range with the exception of triphenyl phosphate (23.5).

Early experience using FPD for both phosphorus and sulfur had been obtained with VX, Sarin and Soman, and subsequently with electron capture (ECD) and FPD for sulfur in the analysis of mustards¹¹. Laboratory effort had been directed, as a continuing study, on the comparative sensitivities of FPD for phosphorus (and sulfur where applicable) as opposed to ECD and FID on a variety of organophosphorus compounds such as parathion, Soman, Sarin and VX.

It was not until finite, side-by-side comparative data were obtained here (*ca.* 1971), that more obvious differences in FPD sensitivity relating the structure became evident.

With some compounds, the lability or relative instability might have been at least a partial explanation for the lesser sensitivity. At that time there had been little experience or opportunity to work with analogous and homologous compounds as related to GC-FPD. When the necessary compounds became available, a screen was set up wherein the common moiety was the dimethylamido group $(\text{CH}_3)_2\text{N}-\text{P}$ (Table II). Looking at this as a family of compounds it can be seen that there is a wide disparity in molar response depending on the nature of the substituents. The rationale employed here was to discover or reject the possibility that $(\text{CH}_3)_2\text{N}-\text{P}=\text{O}$ might not go efficiently to HPO in the flame. As shown in Table II this is certainly not the case. Tabun could be considered as approaching an intermediate level. The high sensitivities of DMAPF2 might be explainable by its volatility as a "slug" to the flame detector, or possibly by the presence of halides as synergists for flame sensitivity, or for some other reason. The amido dichloro compound also showed higher than average sensitivity, but approximately the same as that of methylphosphonodichloridate which is shown later.

The next categorization was as the alkylphosphonates other than O-diester (Table III). This grouping included essentially the phosphonohalidates, and dialkylaminoalkylphosphonates. With the exception of the difluoro compound (MPDF, molar response of 27.0), the methylphosphonofluoridates averaged at 18.24 with Sarin at the low of the halidates (16.8). The lowest values were with compounds containing the dialkylaminoalkyl groups, *i.e.*, VX, 12.8; VM at 10.4, and VO at 9.0. MPDF fits into the sensitivity range of DMAPF2 shown previously in Table II.

The next series of compounds studied against the photometric phosphorus detector were of the morpholinophosphoramidate type (Table IV). The available compounds all showed above average response via FPD. DMMPA and DFMPA were amongst the highest in sensitivity of all the tested compounds, approaching the response of DMAPF2 (Table II).

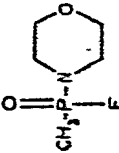
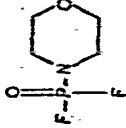
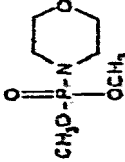
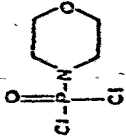
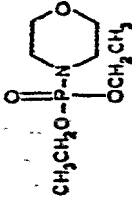
Parathions and paraoxon and some dioxaphosphorinanes were two other

TABLE III
MOLAR RESPONSE TO THE FPD FOR ALKYLPHOSPHONATES OTHER THAN O-DIESTERS

Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_2\text{CH}_2\text{N-(CH}_2\text{CH}_2)_2 \\ \\ \text{OCH}_2\text{CH}_3 \\ \text{O} \end{array}$	VO	2-Diisopropylaminoethyl ethyl methylphosphonate	251	12.35	9.0
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-SCH}_2\text{CH}_2\text{N-(CH}_2\text{CH}_2)_2 \\ \\ \text{O-CH}_2\text{CH}_3 \\ \text{O} \end{array}$	VX	S-2-Diisopropylaminoethyl O-ethyl methylphosphonothioate	267	11.61	12.8
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-OCH}_2\text{CH}_2\text{CH}_2\text{N-(CH}_2\text{CH}_2)_2 \\ \\ \text{F} \\ \text{O} \end{array}$	DMAPMPF	Dimethylaminoethyl methylphosphonofluoridate	183	16.94	9.2
$\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{-P-SCH}_2\text{CH}_2\text{SCH}_2\text{C}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \\ \text{O} \end{array}$		S-2-Ethylthioethyl O-ethyl ethylphosphonothioate	242	12.81	17.2
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-SCH}_2\text{CH}_2\text{SC}_2\text{H}_5 \\ \\ \text{CH}_3 \\ \\ \text{O-CH-C(CH}_3)_2 \\ \text{O} \end{array}$	ETPMP	S-2-Ethylthioethyl O-pinacolyl methylphosphonothioate	284	10.16	18.8
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-F} \\ \\ \text{F} \end{array}$	MPDF	Methylphosphonic difluoride	100	31.00	27.0

$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OCH}_2\text{CH}_3 \\ \\ \text{F} \\ \\ \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OCH}(\text{CH}_3)_2 \\ \\ \text{F} \end{array}$	Ethyl Sarin	Ethyl methylphosphonofluoridate	125	24.60	11.7
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-OCH}(\text{CH}_3)_2 \\ \\ \text{F} \end{array}$	Sarin	Isopropyl methylphosphonofluoridate	140	22.14	16.8
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-O-} \langle \text{Cyclohexane ring} \rangle \text{-O-} \\ \\ \text{F} \end{array}$	Cyclohexyl Sarin	Cyclohexyl methylphosphonofluoridate	174	17.82	18.2
$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ \text{CH}_3\text{-P-OC-C}(\text{CH}_3)_3 \\ \\ \text{F} \quad \text{CH}_3 \\ \\ \text{O} \end{array}$	Soman	Pinacoyl methylphosphonofluoridate	182	17.03	19.0
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-SCH}_2\text{CH}_2\text{N}-(\text{CH}_2\text{CH}_3)_2 \\ \\ \text{OCH}_2\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	VM	S-2-Diethylaminoethyl O-ethyl methylphosphonothioate	239	12.97	10.4
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{-P-SCH}_2\text{CH}_2\text{N}-(\text{CH}(\text{CH}_3)_2)_2 \\ \\ \text{OCH}_2\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	VS	O-Ethyl,S-dii-propylaminoethyl ethylphosphonothioate	281	11.03	9.0
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{-P-SCH}_2\text{CH}_2\text{N}-(\text{CH}_2\text{CH}_3)_2 \\ \\ \text{OCH}_2\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	VE	O-Ethyl,S-diethylaminoethyl ethylphosphonothioate	259	11.97	10.2

TABLE IV
MOLAR RESPONSE OF SOME MORPHOLINOPHOSPHORAMIDATE COMPOUNDS TO THE FPD

Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
	MPMF	Methyl-4-morpholinylphosphoramidic fluoride	167	18.56	23.1
	DFMPA	4-Morpholinylphosphoramidic difluoride	171	18.13	34.7
	DMMPA	Dimethyl 4-morpholinylphosphoramidate	195	15.90	32.0
	DCIMPA	4-Morpholinylphosphoramidic dichloride	203	15.27	23.3
	DEMPA	Diethyl 4-morpholinylphosphoramidate	223	13.90	23.7

categories of pentavalent organophosphorus compound represented in this study. A limited number of the former compounds are discussed here, because the results turned out to be somewhat predictable based on the data obtained in the experiments discussed previously. The dialkylaminoalkyl phosphorinanes which would be expected to show lower sensitivities as do VX and VO, actually gave significantly lower response than the latter two compounds. These data are shown in Table V.

To complete the investigation of compound types a group of available alkylphosphites, including trialkyl- and dialkylhydrogen phosphites, were selected. The former represent trivalent phosphorus; with the latter being capable of behaving as pseudo pentavalent phosphorus compounds. With the exception of triphenyl phosphite, the phosphites exhibited responses at the lower end of the phosphorus ester sensitivity range. This is not surprising since these compounds are in a reduced state and would probably show better response with a more oxidative or richer air-feed combustion. The phosphites studied and the FPD results obtained are shown in Table VI.

An important consideration relative to the sensitivity of a given species to the FPD is obviously one of how much sample actually gets to the detector. This would fall into the category of throughput characteristics of the column and the stability of a compound in the particular substrate. As a test of column variable, three different substrates were selected on the basis of their differences in polarity. The lowest polarity was represented by SE-30, the next highest by OV-17 and the highest by QF-1 (McReynolds constant ratio of 1:5:7). The last is the substrate that was used for all of the work reported in the previous tables. It can be seen in Table VII that polarity of column had no bearing on the stability of these compounds or their throughput, as relates to sensitivity to FPD.

As another approach to understanding possible differences in FPD sensitivity an attempt was made to equate FID as an independent or analogous measure of throughput of compound to the detector. Although uncertainty may yet exist as to the mechanism of ion formation within the flame, it is reasonable to assume that the detector response is directly proportional to the carbon content of the compound and also related to the hydrogen atom¹². Indications have been reported that the presence of alcoholic oxygen on amine nitrogen can reduce the molar response¹²⁻¹⁴.

In our determination, the sum of the atomic weights of carbon and hydrogen in a given molecule were calculated as an atomic ratio and thence as an atomic response.

Atomic number = Sum of atomic weights of carbon and hydrogen

$$\text{Atomic ratio} = \frac{\text{Atomic number}}{\text{Molecular weight of compound}}$$

$$\text{Atomic response} = \frac{\text{FID response/concentration of sample}}{\text{Atomic ratio}}$$

The atomic response, making the assumption that no atoms other than carbon and hydrogen participate in the energetics of flame ionization, should be equivalent to the molar response to FPD. What is found in comparing the atomic response of FID in Table VIII to FPD (Tables I-VI) is that with the exception of VO, TMFO,

TABLE V

MOLAR RESPONSE TO FPD OF SOME *p*-NITROPHENYL PHOSPHATES AND DIOXAPHOSPHORINANS

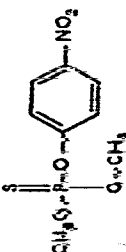
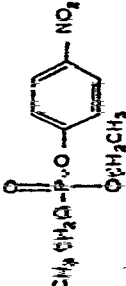
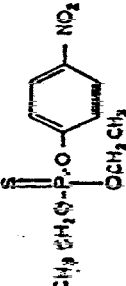




Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
	Methyl parathion	Dimethyl <i>p</i> -nitrophenyl phosphite	263	11.79	19.5
	Parathion	Diethyl <i>p</i> -nitrophenyl phosphite	275	11.27	18.9
	Parathion	Diethyl <i>p</i> -nitrophenyl thiophosphate	291	10.87	20.9
	DEAPDP	O,2-Diethylaminoethyl 2-oxo-1,3,2-dioxaphosphorinane	221	14.03	3.6
	DPAEDP	S,2-Diisopropylaminoethyl 2-oxo-1,3,2-dioxaphosphorinane	281	11.03	3.0
	FDP	2-Fluoro-2-oxo-1,3,2-dioxaphosphorinane	140	22.14	18.4
	DPEADP	O,2-Diisopropylaminoethyl 2-oxo-1,3,2-dioxaphosphorinane	193	16.06	4.2

TABLE VI
MOLAR RESPONSE OF SOME DIALKYL HYDROGEN AND TRIALKYL PHOSPHITES TO THE FPD

Structure	Compound	Systematic name	Molecular weight	Phosphorus (%)	Molar response
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{O}-\text{P}-\text{H} \\ \\ \text{OCH}_3 \\ \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{H} \\ \\ \text{OCH}_2\text{CH}_3 \\ \text{O} \end{array}$	DMHP	Dimethyl phosphonate Dimethyl hydrogen phosphite	110	28.18	14.0
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{H} \\ \\ \text{OCH}_2\text{CH}_3 \\ \text{O} \end{array}$	DEHP	Diethyl phosphonate Diethyl hydrogen phosphite	138	22.45	14.2
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{O}-\text{P}-\text{H} \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{O} \end{array}$	DBHP	Dibutyl phosphonate Dibutyl hydrogen phosphite	178	17.42	15.6
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{O} \end{array}$	TEP	Triethyl phosphite	166	18.67	13.6
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{O} \end{array}$	TBP	Tributyl phosphite	250	12.40	13.3
$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5-\text{O}-\text{P}-\text{O}-\text{C}_6\text{H}_5 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array}$	TPhP	Triphenyl phosphite	310	10.00	18.3

TABLE VII

COMPARATIVE MOLAR RESPONSE TO THE FPD OF SOME SELECTED COMPOUNDS VIA THREE CHROMATOGRAPHIC COLUMNS OF DIFFERENT POLARITY

Compound	Molar response		
	SE-30	OV-17	QF-1
DIMP	20.5	20.8	19.8
DMMP	20.9	21.0	20.5
VX	13.7	13.8	12.8
VO	9.8	9.2	9.0
VM	10.0	10.2	10.4
VS	9.7	10.2	9.7
Sarin	17.2	16.9	16.8

DMMP, DMMPA and DPAEDP, the ratio of FPD to FID gives a mean of 0.56 ± 0.07 . The FPD/FID ratios found for VO and DPAEDP are significantly lower than all of the other compounds. VO should be amongst the most chemically and pyrolytically stable of all of the dialkylaminoalkyl compounds studied. Its FPD response is in the low range as are all of the dialkylaminoalkyl compounds. Its FID atomic response compares favorably with that of the average FPD range compounds (FPD/FID 0.56). This could indicate that VO is reaching the photometric detector. VX is similarly responsive to the FID but also low in FPD response as are the other related compounds in its series. The possibility thus exists that cyclization of the group as the dialkylammonium may have some bearing on the phosphorus sensitivity. The sensi-

TABLE VIII

COMPARATIVE SENSITIVITIES OF SOME SELECTED COMPOUNDS TO THE FID WITH RESULTS FROM THE FPD

Compound	Atomic number	Molecular weight	Atomic ratio (%)	FID atomic response	FPD molar response*	FPD/FID ratio
VO	158	251	62.95	27.3	9.0	0.32
VX	158	267	59.18	26.5	12.8	0.49
VS	172	281	61.21	16.0	9.7	0.61
DFAEDP	156	281	55.51	15.1	3.0	0.20
DMAPMPF	87	183	47.54	16.3	9.2	0.56
VM	130	239	54.39	19.2	10.4	0.54
VE	144	259	55.60	18.8	10.2	0.54
DIMP	101	180	56.11	34.3	19.8	0.58
DMAPF2	30	129	23.25	16.0	39.4	2.46
DEMP	73	152	48.03	26.4	19.6	0.74
DMMP	45	124	36.29	22.2	20.5	0.92
DEEP	87	166	52.41	32.6	20.1	0.62
TMPO	45	140	32.14	17.0	19.9	1.17
TP ₂ PO	129	224	57.59	33.1	20.6	0.62
TBuPO	171	266	64.29	33.4	19.4	0.57
DMMPA	86	195	44.10	30.3	32.0	1.06
DEMPA	114	223	51.12	24.0	23.7	0.99
DFMPA	56	171	32.75	27.5	34.7	1.26

* FPD molar responses from Tables I-VI.

tivities of key compounds by FID, including comparison with FPD, are shown in Table VIII.

Emission spectra were determined on some selected organophosphorus compounds, employing a Perkin-Elmer Model 460 atomic absorption flame emission spectrophotometer. Hydrogen was used as the fuel and argon served as the diluent gas. All of the compounds examined were run at a concentration of 20 mM.

The emission peak for HPO occurs at 525 to 530 nm. Flame emission sensitivity for phosphorus on the flame emission spectrometer was 5 to 6 logs lower than that obtained with the GC-FPD. Selected for this study both as comparative information and because sufficient sample was available were phosphoric acid, methylphosphonic acid $\text{CH}_3\text{PO}(\text{OH})_2$, DMMP, DIMP, 2-diisopropylaminoethyl methylphosphonite (TV) and VO. In water and 0.1 M hydrochloric acid it was found that these compounds all had the same general type of HPO emission peak without the appearance of significant P bands other than at 526 nm. In 0.1 M hydrochloric acid the peak height appeared to increase, in some cases, with increasing molecular weight, although an insufficient number of compounds or variety of structure were measured to consider this a fact. The addition of organic solvents (methanol, for example) in 10% or greater quantities caused the HPO peak to disappear. Sodium pyrophosphate gave no HPO peak either in water or in 0.1 M hydrochloric acid.

Because of the limitations in the atomic absorption flame emission equipment, the experiments could not be made to duplicate those of the FPD. The data relating peak height at 526 nm to molarity of compound are shown in Table IX. It should be understood that the flame emission study differs from GC-FPD in that all of any compound is aspirated into the flame. In the case of VO this might indicate, in part, that less of the compound reaches the detector in GC-FPD thus explaining its lower sensitivity by that route. However, other factors have to be involved when compared with lower values for DIMP and DMMP. It is not believed that sufficient evidence was obtained by flame emission measurement to support a conclusion that less of the lower sensitivity compounds reach the detector. It is more than coincidental that all of the dialkylaminoalkyl phosphonates are in the low class of sensitivity. With only few exceptions all are capable of cyclizing at the aminoalkyl group which could have a limiting effect on behavior at the detector. These emission results are shown in Table IX.

TABLE IX

FLAME EMISSION SPECTROPHOTOMETRY OF SOME SELECTED PHOSPHORUS COMPOUNDS (MEASUREMENT OF 526 nm EMISSION)

<i>Compound</i>	<i>Molecular weight</i>	<i>Peak height (cm/mM)</i>
H_3PO_4	98.0	0.175
$\text{CH}_3\text{PO}(\text{OH})_2$	96.0	0.306
DMMP	124.0	0.196
DIMP	180.2	0.450
TV*	235.2	0.811
VO	251.3	0.647

* TV = 2-Diisopropylaminoethyl ethyl methylphosphonite. Its molar response to the FPD is 9.7 which is close to the 9.0 of VO.

As a last consideration but still related to potential throughput of compound to detector is retention time in the chromatographic column. The retention index¹⁵ of a compound relates its GC retention time with that of a series of straight-chain hydrocarbons. The higher the retention index of the compound, the longer is its residence time in the chromatographic column. Comparing the FPD results of some of the compounds shown above with the same QF-1 column, but at an isotherm of 190° and thermal conductivity detection, some interesting relationships are found. First of all it is evident that no direct correlation is seen that would relate FPD molar response either to the inverse of, or directly to retention index. The retention index has no units which are related to sensitivity to the TCD nor to the FID. Instead, retention index (R_I) has units which are only related to time in the heated chromatographic column (190°). If an inverse relationship of molar response to R_I (including TCD sensitivity measurement) had been obtained it might have been indicative of decomposition, or efficiency of column throughput. These results are summarized in Table X.

TABLE X

COMPARISON OF MOLAR RESPONSE TO FPD WITH RETENTION INDICES

The retention index was determined using a 10% QF-1 column at an isotherm of 190°. Detection was by TCD and in some compounds by FID.

<i>Compound</i>	<i>Retention index</i>	<i>Molar response</i>
Sarin	1300	16.8
Soman	1567	19.0
Tabun	1800	17.1
Cyclohexyl Sarin	1770	18.2
DPMP	2055	20.2
DIMP	1757	19.8
DEMP	1550	19.6
VX	2185	12.8
VO	2190	9.0

A thermionic NPD¹⁶ was obtained and used in the latter stage of this study. Since the NPD is sufficiently different in operation than the FPD it was hoped that some fundamental comparative information might result. Although more sensitive for phosphorus detection than the FPD the comparative molar responses between the two detectors were quite similar. These results are shown in Table XI. Arbitrarily it might be assumed that these data are indicative of lower throughput of the dialkyl-aminoalkyl phosphonates. However, this could be coincidental based on some of the known behavior of some of these compounds.

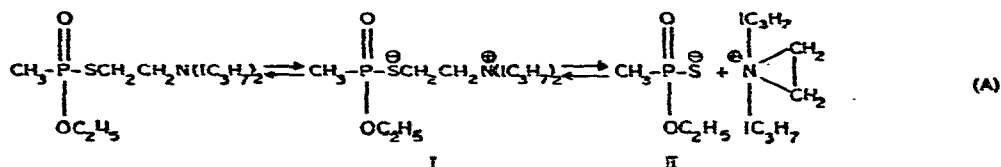
Critical analysis of the previously described investigative data leads to a number of premises ranging from the more obvious to the still postulated. Sufficient information has been obtained to establish that within a given homologous series, FPD sensitivity can be linear with respect to molar content of phosphorus. It is also safe to presume that this molar relationship of phosphorus content to FPD sensitivity does not predictably hold for mixed analogous and homologous compounds.

It should be stated that in our FID studies we did not encounter the negative interferences from the presence of alcoholic oxygen or amine nitrogen that have been

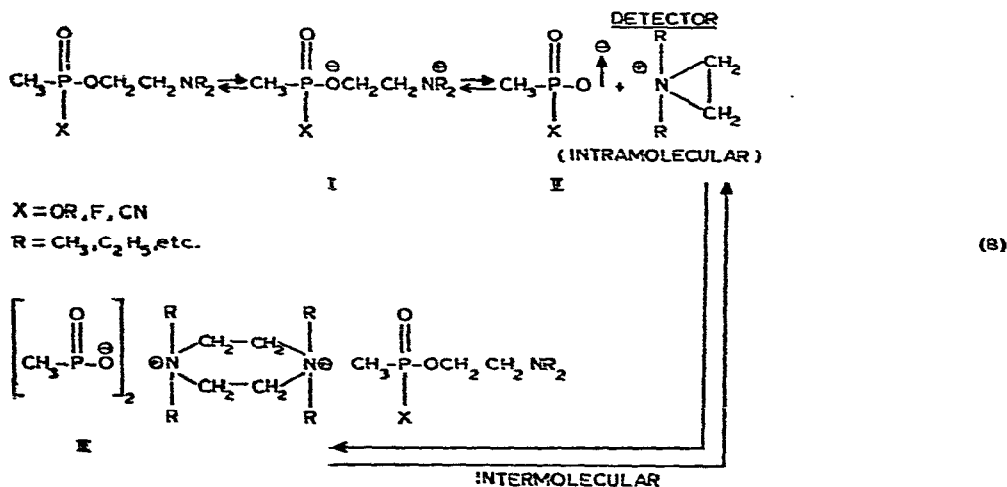
reported by others¹²⁻¹⁴, either from the phosphoramidates or the dialkylaminoethyl phosphonates. Nor is there evidence that the geometry or gas mixture⁶ is responsible for our observed lesser sensitivities of the latter group of compounds at the FPD.

From all of the foregoing experimentation and discussion, it is a fact that the structure of an organophosphorus compound can have a bearing on its FPD sensitivity. Molar response to FPD is found to be relatively linear in the case of phosphorus diesters and triesters, phosphofluoridate esters, phosphoramidates of the alkyl fluorides and cyanides, and a fluorophosphorinane.

In general, all of the straight-chain dialkylaminoalkyl phosphorus compounds appear to be in a class to themselves and can be fitted into a molar response pattern of their own. It is a known fact that these species have shown to a greater or lesser extent the characteristics of intra- and/or intermolecular reaction to form aziridinium of piperazinium salts, respectively, not unlike the nitrogen mustards. In the gas phase, formation of the aziridine salt (intramolecular) might be expected to be more likely than the piperazine salt but both could be possible. Using VX as the example, the reaction may be illustrated as follows:



Selecting VO as the example, several possibilities exist as illustrated below. The group represented by X could be OR, F, or CN. The R groups could be CH₃, C₂H₅ and higher.



Whereas reactions such as these could conceivably occur in the GC column as well as at the FPD the same effect should be observable via response from the FID. Referring to Table VIII, it is seen that with only few exceptions the FID atomic response approaches twice that of the FPD molar response for the aminoalkyl compounds.

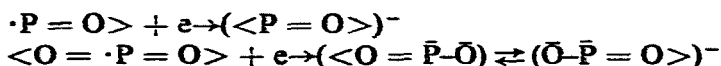
TABLE XI
COMPARISON OF FPD VERSUS NPD (PHOSPHORUS MODE) ON SOME SELECTED PHOSPHONATES

Compound	Molar response	
	FPD	NPD
DIMP	19.80	20.1
DMMP	20.5	21.6
Sarin	16.8	17.5
Tabun	17.1	18.3
VO	9.0	10.7
VX	12.8	13.4

Not ignored is the possibility of systemic conversion of the quaternary amines to volatile amines with subsequent response in the FID, while phosphorus does not reach the FPD or NPD. Whether the charged salt is just a concept or the actual mechanism at the detector for explaining the difference in FPD response, it is nonetheless worth mentioning here. Proof of this concept would require preparation of the cyclized species and redesign of the gas chromatograph to allow direct feed to the detector.

On the basis of the FPD/FID ratios and the similarity of results obtained via the thermionic NPD along with independence from polarity of column, it would appear that the response to FPD is a direct function of the substituents on the phosphorus atom. The response to FPD and NPD could be attributable to the species of ion that approaches and is formed in the detector.

The FPD measures the HPO formation as a radiation due to electronic excitation. The NPD is speculated to depend on the formation of PO or PO₂ as intermediate radicals, being net negative ions drawn to a positively charged collector¹⁶, as illustrated in the following equations:



The lower responses obtained via NPD for the dialkylaminoalkyl compounds (VX, VO, and similar compounds) can be explained from eqns. A and B as the effect of a mixture of species in which form I above gives little or no response at the FPD or NPD while either the unchanged forms or II and III (the dissociated forms) are essentially responsible for all of the detection.

We have arbitrarily assigned those organophosphorus compounds which showed FPD responses of 20 ± 3 to a "normal" range. Those compounds which approach half or less of the "normal" in response we place in the lower sensitivity grouping, i.e., VX (12.8) VO (9.0) DPAEDP, etc.

Those compounds showing more than twice that of the 16.8 of Sarin, like DMMPA (32.0) DMAPF2 (39.4), etc. are less easily explained. This latter group, some of which are dihalides and others not, have little in common based on all of the forgoing tests. It is evident that the difluoro (and dichloro) compounds give "high" responses via FPD, whereas, the monofluoro compounds are average or slightly lower.

REFERENCES

- 1 S. Brody and J. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.
- 2 H. Draeger and B. W. Draeger, German Pat. 1,133,918 (1962).
- 3 M. Bowman and M. Beroza, *J. Ass. Offic. Anal. Chem.*, 49 (1966) 1154.
- 4 M. Bowman and M. Beroza, *Anal. Chem.*, 40 (1968) 1448.
- 5 H. W. Grice, M. L. Yates and D. J. David, *J. Chromatogr. Sci.*, 8 (1970) 90.
- 6 J. Sevcik and Nguyen thi Phuong Theo, *Chromatographia*, 8 (1975) 559.
- 7 L. K. Beach and S. Sass, *Anal. Chem.*, 33 (1961) 901.
- 8 S. Sass, P. M. Davis, C. J. Cohen, T. Mason and N. Beitsch, *Chem. Warf. Lab., Report 2225* (internal report), Chem. Syst. Lab., Aberdeen Proving Ground, Md., July 1959.
- 9 S. Sass, S. Pinsky, T. L. Fisher and M. R. Barnes, unpublished results.
- 10 S. Sass, N. Beitsch and C. U. Morgan, *Anal. Chem.*, 31 (1959) 1970.
- 11 T. L. Fisher, M. Jaskot and S. Sass, *Edgewood Arsenal Technical Report 4321*, Chem. Syst. Lab., Aberdeen Proving Ground, Md., July 1969 (literature report in preparation).
- 12 J. C. Sternberg, W. S. Gallaway and D. T. L. Jones, in N. Brenner, J. E. Callan and M. D. Weiss (Editors), *Gas Chromatography*, Academic Press, 1962, p. 231.
- 13 A. T. Blades, *J. Chromatogr. Sci.*, 11 (1973), 251.
- 14 C. J. O. R. Morris, *Lab. Pract.*, 23 (1974) 513.
- 15 E. sz. Kovats, *Advan. Chromatogr.*, 1 (1965) 229.
- 16 B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1974) 625.