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PHOSPHORUS-SENSITIVE DETECTORS FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

I. MODIFICATION OF A TRANSPORT FLAME IONIZATION DETECTOR TO THE THERMAL IONIC DETECTOR MODE

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SUMMARY

We describe a simple modification of a high-performance liquid chromatographic transport class detector, the Pye Unicam flame ionization detector (FID), which enables selective detection of organophosphorus compounds. The modification described involves conversion of the existing FID to a thermal ionic detector (TID) by addition above the FID of a rubidium silicate glass bead. The bead can be electrically heated by an externally controlled source to allow adjustments to the bead's background ionization current which determines the sensitivity of the detector. Enhanced sensitivity as well as selectivity for phosphorus over hydrocarbon responses is expected for any detector of the TID class, and this modification should aid analysts interested in detecting and quantitating organophosphorus compounds in complex matrices.

INTRODUCTION

Since Karmen and Giuffrida[1] first described a hydrogen flame doped with alkali metal vapor as being sensitized to phosphorus, numerous variations of this class of gas chromatographic detector have been reported[2]. The thermal ionic detector (TID) described here is of the rubidium silicate variety which is reported to give relative ease of operation[3–5]. A description of this type of TID[3,4], its possible mechanism[5] and investigations of its operating parameters[6] have been described. Also, a study of the composition of the essential element of this detector, the glass bead, has been presented[7–9].

Julin *et al.*[10] developed a phosphorus- and sulfur-sensitive detector for high-performance liquid chromatography (HPLC) not requiring a transport interface. They utilized a special burner and monitored the HPO (Salet phenomena) and S_2 emission with a filter photometer. The detector was utilized for the assay of 5'-monophosphate nucleotides but was limited to reversed-phase solvent systems since

emission quenching, CH_2 background interference and soot formation were all associated with high concentrations of hydrocarbon solvents at such low flame temperatures. Owing to the transport mechanism the detector described in this communication is compatible with all solvent systems.

Šlais and Krejči[11] have described a similar system of HPLC–TID using a totally redesigned two-stage burner–detector system and Balaukin et al.[12] described a detector where the wire was transported through the TID flame. The former detector was used to detect halogen derivatives of tetrahydrofurans but both detectors required totally redesigned burner systems in order to allow the detectors to operate as TIDs.

The modification described here can be applied to any existing flame ionization detector (FID) of similar configuration to the Pye Unicam FID (Pye Unicam, Cambridge, Great Britain) and requires no permanent modification of the FID. In fact, interconversion from the TID to FID requires only about 5-min time. Also, by proper adjustment of the bead height, hydrogen and air flow-rates, the detector should be sensitive to nitrogen- and sulfur-containing compounds[3-6].

MATERIALS AND METHODS

The modified Pye Unicam FID described here is shown in Fig. 1. It consists of an electrically insulated burner with permanent nozzle, a cylindrical collector electrode assembly maintained in position by a ceramic disk and a glow plug igniter. An exit port is located next to the glow plug igniter. The addition to the FID which
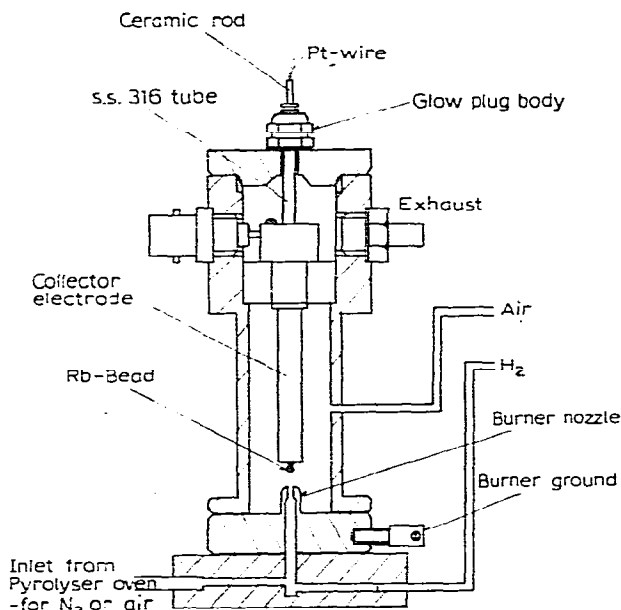

Fig. 1. The modified Pye Unicam FID. Additions made were the ceramic rod, stainless steel 316 (S.S. 316) tube of bead holder, rubidium silicate bead (Rb-Bead) and platinum wire (Pt-wire) leading to the Rb-Bead. Figure modified from LC Technical Manual (System 2) with permission from Pye Unicam.

converts it to a TID is the bead holder and rubidium silicate bead, the bead holder extending from the glow plug body through the collector electrode in such a way that the bead is positioned above the burner nozzle.

Nitrogen or air is used to purge the pyrolysis oven of the moving-wire portion of the detector and is premixed with hydrogen before introduction to the burner. Air is introduced to the detector through a side port in the detector body. The introduced air sweeps down to the burner from the exterior portion of the collector electrode and then up through the center of the electrode along with exhaust products from the burner.

In modifying the FID to a TID, placement of a rubidium silicate bead over the burner is necessary. This is accomplished by converting the existing glow plug body of the FID, which is centrally located over the burner, to a bead holder. Also, the bead holder described allows use of an externally applied current to heat the bead and thus gives flexibility in generating the ionization background current (i_{BC}) important to the sensitivity of this detector[3-7].

With reference to Fig. 1, the necessary modifications made to the glow plug are: (1) the attachment of a 4.3-cm-long 316 stainless-steel tube (0.47 cm O.D., 0.28 cm I.D.) to a glow plug body; (2) the placement of a 7.5-cm-long ceramic rod (0.275-cm O.D., Omegatite 350 two-hole round thermal-couple insulator, Model TRAO4018, Omega Engineering) containing two parallel bores through this stainless-steel tube and (3) the threading of a 18-cm-long, 0.5-mm diameter platinum-wire (Fisher Scientific, Pittsburgh, Pa., U.S.A.) through the bores in the ceramic rod in such a way that a 3-mm loop is left at one end of the ceramic rod. To this loop is attached the rubidium silicate bead (see below).

With the tubing size used in constructing the bead holder the holder is able to fit through the collector electrode and is held in place by the glow plug body. The bead height above the burner is adjusted by sliding the ceramic rod with respect to the stainless steel mounted into the stainless-steel tubing and glow plug body. An Allen screw is used to secure the position of the rod once an optimum height of bead above the burner is attained. In this study the rubidium bead is placed 5 mm above the burner. This region corresponds to a flame temperature zone of 700–800° (depending on flame conditions) as measured with a differential thermocouple (10-560-10, Fisher Scientific).

To be certain that no collector area will be below the level of the bead, 1 cm of the collector electrode is removed. In this way separation of FID from TID response is assured[13,14].

To heat the bead electrically, two in parallel 10-A maximum Powerstats (Superior Electric) are used and connected to the platinum leads extending from the ceramic rod above the glow plug body. One Powerstat is used for coarse and the other for fine adjustment of the bead heating current (i_B). A Wilbac Model ACA15 0–15-A AC ammeter is used in series with the Powerstats to monitor applied current. Also, voltage to the Powerstats is stabilized by using a Type CVH Sola constant voltage transformer. A maximum of 10 A can be applied to heat the bead.

The final modification involves the burner polarizing voltage (-170 V) delivered from the Pye Unicam ionization amplifier. A 4-pole double-throw switch is used to connect the polarizing voltage and ground, so that in one direction the burner is at ground and the platinum lead to the bead is polarized. This is necessary

since polarization of the bead is the normal TID configuration[3,5]. For FID operation the bead is removed and the switch thrown in the other direction, thus polarizing the burner.

The Pye Unicam ionization amplifier and dual-temperature controller are used to monitor the response from the detector and maintain constant pyrolysis and detector oven temperatures, respectively. The solvent evaporator oven of the moving-wire detector is not used, the detector oven is maintained at 200°, and the pyrolysis oven temperature is varied when appropriate.

A Honeywell Electronik 196 (10 mV FSD) recorder is used to record the amplifier output responses and noise measurements.

The alkali metal source, a rubidium silicate glass bead, was fabricated according to Lubkowitz et al.[7,8]. Since they mentioned that a more complete study was underway to optimize the composition of the alkali source, only one bead composition was used. The bead contained 17 % (w/w) rubidium chloride to Corning 7740 glass (Pyrex). Ground glass and rubidium chloride were mixed and placed in a 15-ml Coors porcelain crucible. While stirring continuously with a quartz rod, a butane-oxygen rich flame was used to melt the mix. Once a melt was formed a strand was pulled and, using a smaller flame, attached to the bead holder platinum wire loop. One bead, 1.9 mm diameter, was used for this entire study. Once attached and centered on the wire the bead was aged glowing red in the flame for 10 min and then annealed for another 10 min in a sooty flame. After placement in the detector, a high bead heating current (9.0 A) was applied through the bead until a stable ionization background current was attained (approximately 5 h). A properly aged bead should give a i_{BC} of around 1 pA at high bead current[7], i.e., enough to cause the bead to glow red.

The evaluation of the detector involved first relating the rubidium silicate bead response to variations in hydrogen, air, and nitrogen flow-rates and bead heating current. Since the Pye system did not provide an adequate means of quantitating gas flow-rates, Brooks flow controllers and rotameters (Emerson Electric) were used. These were modified for the flow-rate ranges used. All gases were of "Zero Gas" purity (Linde Specialty Gases, Union Carbide Canada, Toronto, Canada) and further purified by passing through filters of Drierite (Anachemia Chemicals, Montreal, Canada) and Type 3A molecular sieve (Matheson, Coleman & Bell, Norwood, Ohio, U.S.A.). At a constant i_B evaluation of the bead response involved varying the hydrogen, air or nitrogen flow-rate while keeping the other two rates constant and measuring i_{BC}. These measurements were repeated at different bead heating currents.

To evaluate the response of the detector to selective standards, samples in a 0.5 ml/min methanol (Spectrograde; American Chemicals, Montreal, Canada) stream were delivered to the coating block of the moving-wire portion of the detector with a Model 396 Milton Roy Minipump (Laboratory Data Control), home-made pulse damping system[15] and a Valco 3000 p.s.i.g. valve with 20-μl sample loop. As an substitute for a column, 4 ft. of connecting tubing (1/16 in. O.D., 0.030 in. I.D.) were used between the injector and detector to allow some band broadening.

The standards evaluated were reagent-grade chloro- and nitrobenzene (Fisher Scientific), aniline and octanoic acid (Baker Analyzed Reagent; J. T. Baker, Phillipsburgh, N.J., U.S.A.), hexadecane (Eastment Organic Chemicals, Rochester, N.Y., U.S.A.), tri-n-butyl phosphate (Fisher Scientific), L-α-distearoyl phosphatidylcholine

(Sigma, St. Louis, Mo., U.S.A.) and organophosphorus pesticides (Supelco, Bellefonte, Pa., U.S.A.). Working standards were made of chloro- and nitrobenzene, aniline, octanoic acid and hexadecane to correspond to a 10-mg sample delivered to the detector coating block. These roughly corresponded to 10 ml of standard in 15 ml of hexane (Spectrograde; American Chemicals). Tri-*n*-butyl phosphate and phosphatidylcholine solutions were made with methanol to correspond to a 20-mg sample delivered to the coating block while the pesticides were as 50% solutions in methanol (Spectrograde; American Chemicals). The malathion standards for the evaluation of linearity and sensitivity of the detector were made by appropriate serial dilution in methanol.

RESULTS

While this detector is similar in principle to a previously described detector[3–5], it varies considerably in burner design. A series of experiments was conducted to compare the operating parameters (i_B, and nitrogen, air and hydrogen flow-rates) of the present detector with a similar study reported for the previously described detector. The detectors were not expected to be directly comparable but general similarities were expected to be found.

Lubkowitz et al.[6] found i_{BC} to be a function of bead heating current, and as the bead aged greater i_B was required to attain the same i_{BC}. Fig. 2 shows i_{BC} versus i_B for our bead. As can be seen, a significant decline in i_{BC} was observed after 10 days usage. The i_B required to attain a given i_{BC} was significantly higher in our system, presumably owing to the large bead size used and the necessity of heating the bead holder.

The dependence of i_{BC} on nitrogen, hydrogen and air flow-rates was also investigated. This was done because the sensitivity of the TID is a function of i_{BC} and numerous ways of attaining the same i_{BC} are possible. Figs. 3A, B and C show that a different dependence of i_{BC} was observed for nitrogen, air and hydrogen at different
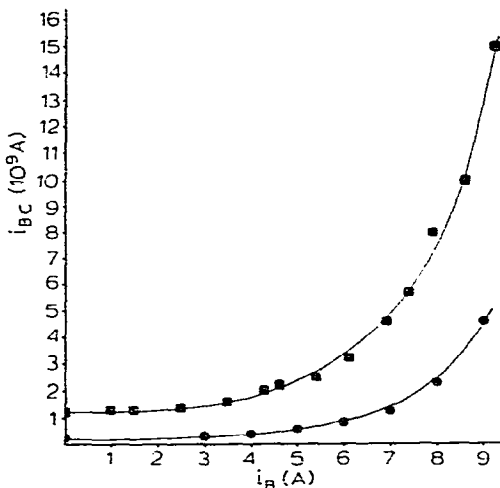

Fig. 2. Plot of i_{BC} versus i_B for two separate days. ■—■, day 1; ●—●, day 10. Air = 590 ml/min, hydrogen = 35 ml/min, nitrogen = 30 ml/min, detector oven = 200°.

i_B. For nitrogen flow-rates from 0 to 34 ml/min (Fig. 3A) the effect was not dramatic and, as expected from a previous study[6], at increasing nitrogen flow-rates i_{BC} was observed to decrease. The reason for this decrease is not known but has been attributed to cooling of the bead by convection[6]. Using a platinum–platinel thermocouple, we measured an increase in the temperature of the zone where our bead was placed. This observation warrants further investigation.
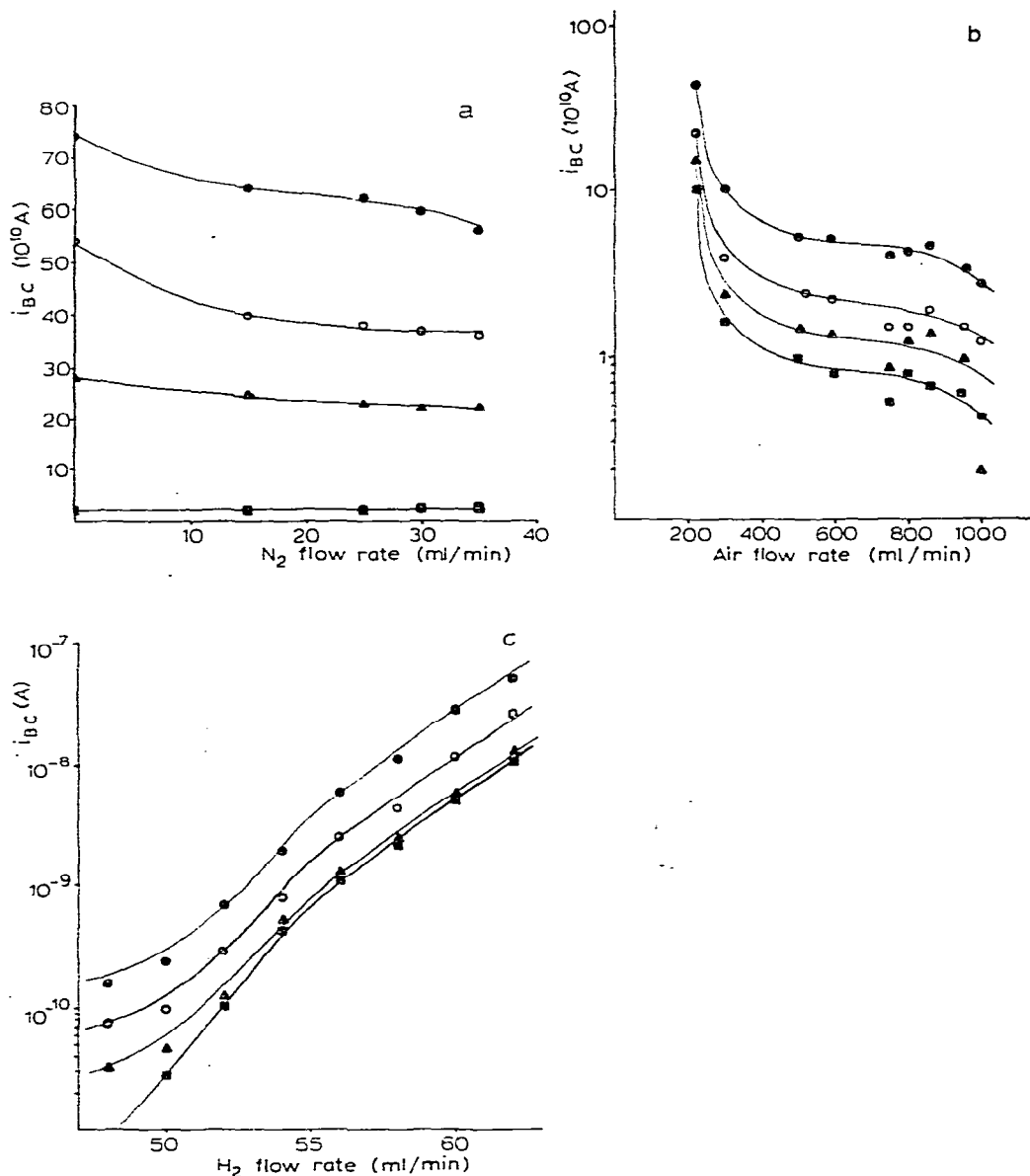

Fig. 3. i_{BC} as a function of changes in (a) nitrogen, (b) air and (c) hydrogen flow-rate and bead heating current. Unless otherwise stated, hydrogen = 51 ml/min, air = 300 ml/min and nitrogen = 35 ml/min. ●—●, i_B = 0; ○—○, i_B = 3 A; ▲—▲, i_B = 5 A, ■—■, i_B = 7 A.

Fig. 3B shows that by increasing air flow-rates from 220 to 1000 ml/min, ionization decreased more significantly than for nitrogen changes over its entire range. The nitrogen flow-rate was normally left constant at 30 or 35 ml/min while the air flow-rate was varied from 300 to 500 ml/min. For nitrogen a high flow-rate is required to prevent tail skewing of injected samples. Air flow-rates have the similar effect of preventing misshaped peaks and so must be maintained at a rather high value.

Fig. 3C shows that hydrogen flow-rates from 48 to 64 ml/min play the most significant role of the three. As expected an increasing hydrogen flow-rate increased i_{BC} due to direct heating. What was unexpected was how large a dependence i_{BC} had on the hydrogen flow-rate. Fig. 3C indicates that very careful control of the hydrogen flow-rate is required to prevent considerable low frequency noise. Because the ionization process responsible for maintaining i_{BC} (*i.e.*, rubidium loss from the bead) occurs on the bead surface, fluctuations in the hydrogen flow-rate are expected to make a greater contribution to noise than i_B. The bead heating current heats through the center of the bead, where the bead heat capacity can buffer any short term fluctuations in current. A voltage stabilizer for the bead heater is still required since line voltage fluctuations, without the stabilizer, cause significant low frequency fluctuations in i_{BC} and baseline drift at low attenuations.

The gas flow-rates used in these studies represent the upper and lower limits of combustion with the burner system used and are quite different than those given in the comparison study[6]. This is expected because of the totally different burner designs employed by the Pye and Perkin-Elmer systems.

Selectivity

One problem associated with evaluating a TID using a wire-transport interface is the uncertainty of the amount of sample reaching the detector[11]. In order to test the selectivity of this modified detector the transport mechanism was first run with the FID in place. Nitrogen was used as the purge gas from the pyrolysis oven for nitrobenzene, chlorobenzene, aniline, *tert.*-butyl phosphate, hexadecane, octanoic acid and phosphatidylcholine. The results are presented in Table I. As indicated by

TABLE I

COMPARISON OF FID TO TID RESPONSES FOR STANDARDS

N.R. no response above noise. Hydrogen = 32 ml/min; air = 590 ml/min and nitrogen = 35 ml/min. Wire speed = 6 cm/sec, pyrolysis oven = 700°.

Standard	FID response (A)*	TID response (A)	
		Air**	Nitrogen
Hexadecane	$2 \cdot 10^{-9}$	$1.1 \cdot 10^{-12}$	$2.8 \cdot 10^{-10}$
Octanoic acid	$1.2 \cdot 10^{-9}$	$1.3 \cdot 10^{-12}$	$1.4 \cdot 10^{-10}$
tert.-Butyl phosphate	$1.3 \cdot 10^{-9}$	$1.5 \cdot 10^{-11}$	$1.0 \cdot 10^{-10}$
Chlorobenzene	N.R.	N.R.	N.R.
Nitrobenzene	$3 \cdot 10^{-13}$	N.R.	N.R.
Aniline	N.R.	N.R.	N.R.
Phosphatidylcholine	$5 \cdot 10^{-10}$	N.R.	$7.5 \cdot 10^{-10}$

  * See text for sample amounts.
  ** Air was substituted for nitrogen as purge gas from pyrolysis oven.

Šlais and Krejčí[11] the response from a detector of this sort is complicated by the wire-transport system, pyrolysis process and gas phase transfer of pyrolysis products to the sensing element. All results in Table I corresponded to injections of a 10-mg sample except for tert.-butyl phosphate and phosphatidylcholine which were 20 μg; peak heights rather than areas were cited since no columns were used. For comparison to the other standards, the tert.-butyl phosphate and phosphatidylcholine responses were multiplied by a factor to correspond to an injected sample of 10 mg.

The FID and TID responses for chlorobenzene, aniline and nitrobenzene were either not detectable or very small. It was assumed that a lack of wire coating was the main reason that these compounds were not detectable. For the FID mode, hexadecane, octanoic acid and tert.-butyl phosphate gave approximately equal responses while phosphatidylcholine gave a slightly reduced response compared to the three detectable standards. The i_{BC} used to generate the data in Table I was $8 \cdot 10^{-9}$ A. Using nitrogen as purge gas and the TID mode, tert.-butyl phosphate and phosphatidylcholine gave responses approximately equal in magnitude to the non-phosphorus-containing standards, hexadecane and octanoic acid.

To investigate further the similarity of response between the non-phosphorus-containing and phosphorus-containing standards, a study involving FID and TID response as a function of pyrolysis oven temperature was conducted. As illustrated by Fig. 4, the response of tert.-butyl phosphate in the FID and TID modes was found to be dependent on pyrolysis oven temperature. As the pyrolysis oven temperature was increased, response in the FID mode increased slightly, while TID response decreased significantly (over 140 times). At 400°, octanoic acid and hexadecane gave no response above noise with the TID detector. Also, the phosphatidylcholine response did not increase with a decrease in oven temperature. Thus it was concluded that for relatively volatile standards such as hexadecane, octanoic acid and tert.-butyl phosphate, compared to phosphatidylcholine, a large portion of the sample coated
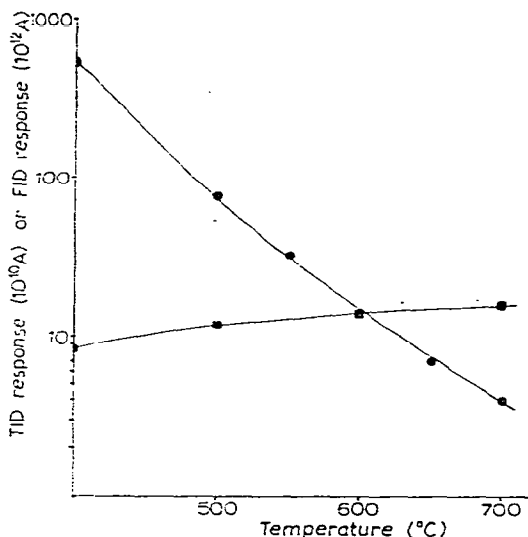

Fig. 4. Detector response as a function of pyrolysis oven temperature, for 20 μg tert.-butyl phosphate. ●—●, TID; ■—■, FID: Hydrogen = 35 ml/min, air = 590 ml/min, nitrogen = 35 ml/min, and wire speed = 6 cm/sec.

on the wire can be transported to the detector sensor. Some compounds such as nitrobenzene, chlorobenzene and aniline were not detectable, apparently owing to a transport problem. Furthermore, the detector is species selective for phosphorus. Care must be taken in controlling pyrolysis oven temperature as too high a temperature appears to be associated with a transport problem to the TID sensor, possibly by formation of some refractory phosphate species.

High-molecular-weight compounds such as phospholipids were not detectable at low levels presumably owing to their low vapor pressure. The low vapor pressure of phosphatidylcholine necessitated high pyrolysis oven temperature, causing the same transport problem associated with *tert.*-butyl phosphate.

The response of organophosphorus pesticides was also tested. These compounds are similar to *tert.*-butyl phosphate, the model compound used to develop this detector. The response of the pesticides tested is given in Table II as a TID–FID ratio. The enhanced sensitivity for this class of compounds indicates again that a relatively high vapor pressure (compared with phophatidylcholine) is necessary for response. Pyrolysis oven temperature was 500° for this study, but could be optimized for any given pesticide of interest.

TABLE II

COMPARISON OF FID TO TID RESPONSE FROM ORGANOPHOSPHORUS PESTICIDES

Sample	Response TID/FID
DDVP	367
Diazion	182
Phorate	252
m-Syston	200
Malathion	219
Parathion	167
Valed	476
Di-syston	238
Phosdrin	222
Ethion	243

Sensitivity

The original purpose for detector modification was the determination of phospholipids in serum samples. As modified, the detector is incapable of any enhanced sensitivity over the Pye Unicam LCM2 system[16,17] for this class of compounds for reasons cited previously. However, the detector may be useful for other classes of organophosphorus compounds, such as pesticides. Therefore, the sensitivity of this detector for malathion was studied. The relationship of response to background ionization for the TID is well documented[6,18,19]. Fig. 5 illustrates that while the signal does increase with an increase in i_{BC}, the *tert.*-butyl phosphate noise also increases. The signal-to-noise ratio (S/N) curve illustrates that an optimum S/N is obtained at lower i_{BC}. For this study i_{BC} was varied by changing the bead current i_B; however, i_{BC} could also be changed by varying the hydrogen for air flow-rate. Lubkowitz et al.[6] illustrate the signal and noise dependence of this type of detector on hydrogen, air, nitrogen and i_B.

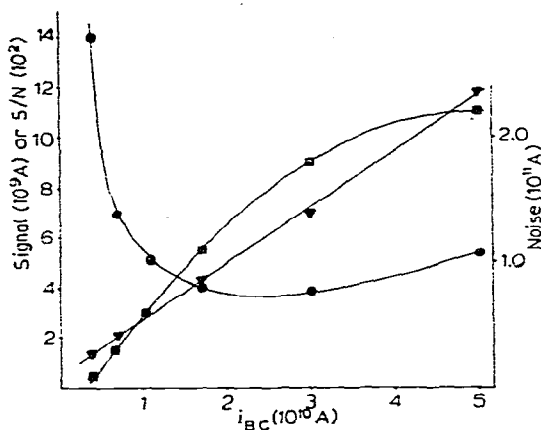Optimization of hydrogen, air and i_B as well as wire speed, which also affects

Fig. 5. TID response, noise and signal-to-noise ratio (S/N) for 20 μg tert.-butyl phosphate as a function of varying i_{BC} by changing bead current. ▼—▼, response; ■—■, noise; ●—●, S/N. Nitrogen = 35 ml/min, hydrogen = 51 ml/min, air = 300 ml/min, wire speed = 6 cm/sec and pyrolysis oven temperature = 600°.

sensitivity and noise, can be done but require a complicated optimization format. No such technique was applied here. When this detector is to be used for quantitating a specific solute, simplex optimization[20],[21] will be employed. Thus the responses given are not optimum with respect to the S/N.

In Fig. 6 is plotted amount of malathion injected *versus* response as peak height. As can be seen the response of the modified detector is linear over at least four orders of magnitude; the detector has the capability of detecting 35 ng of malathion. The detection limit is defined here as the amount of malathion producing a signal twice the peak-to-peak noise as measured over three times the peak base
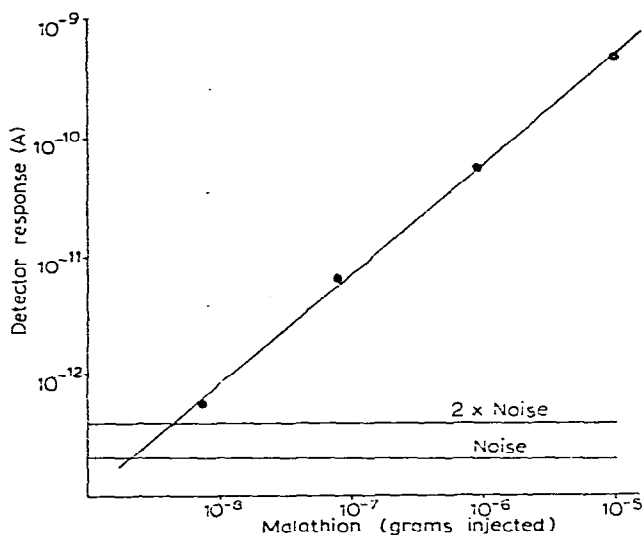

Fig. 6. Responses of the TID to varying amounts of malathion. Conditions as in Fig. 5 with pyrolysis oven temperature 500° and i_{BC} of $3.5 \cdot 10^{-11}$ A.

width. Similar detection limits are expected for the other pesticides monitored as well as other organophosphorus compounds exhibiting some volatility.

DISCUSSION

The objective of this study was to modify a simple transport FID to give enhanced sensitivity for organophosphorus compounds. The data in Figs. 3A, B and C illustrate that different burner configurations require different operating ranges for hydrogen, air and carrier gas (purge gas, nitrogen) flow-rates. Also, the sensitivity of i_{BC} to varying hydrogen flow-rates was greater than expected, and demonstrates that the hydrogen flow-rate must be controlled more carefully than either the air or the purge gas flow-rate. Finally, while bead current i_B can be used to establish a given i_{BC}, the hydrogen flow-rate has a larger effect and must be used initially to establish the lower limit of i_{BC}.

The sensitivity and selectivity of the detector were difficult to evaluate and could not be compared with other reported gas chromatographic detectors because of the different transport mechanism. The response of the detector was due to two phenomena: transportation of the solute to the detector sensing element and response of the sensing element. When compared to an FID using the same transport mechanism, the TID showed enhanced sensitivity for certain organophosphorus pesticides ranging up to 500 times (and presumably greater if properly optimized). The detection of phospholipids by this detector was not possible. This was primarily because of the inability of the transport mechanism to transport the most important portion of the molecule, the phosphate diester, into the flame.

The transport mechanism used here was first devised by James et al.[22] and the entire detector was later improved significantly by Scott and Lawrence[23] with the addition of a reduction unit before the FID which converted the oxidation products from the pyrolysis oven to methane. This later model (not used here) is useful as a detector for hydrocarbon species but detection limits for phospholipids below one microgram are not possible[18,19].

An additional modification to circumvent the transport problems observed with phosphatidylcholine would be to place the transport wire through the TID flame as done by Balaukin et al.[18]. This configuration is presently under investigation. Such a modification would make the detector less useful as a FID detector due to increase in noise[24]. A return to this type of transport system[24] will be necessary for quantitating high-molecular-weight organophosphorus compounds.

ACKNOWLEDGEMENTS

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