PHOSPHORUS RESPONSE MODE OF THE THERMIONIC RUBIDIUM SILICATE DETECTOR

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SUMMARY

In the phosphorus mode, a thermionic rubidium silicate detector gave a response of $2 \cdot 10^{-3}$ C/g for azobenzene, revealing an unexpectedly high sensitivity toward a nitrogen-containing compound. Depending upon detector conditions, the detector could be made from 15 to 120 times more sensitive for malathion, a phosphorus-containing compound, than for azobenzene. The dependence of sensitivity upon carrier-gas flow was complex. Sharp maxima in sensitivity were exhibited at total detector gas flows of approximately 70 ml/min. For the insecticides dursban, diazinon and methyl parathion, each of which contained both phosphorus and nitrogen, the predominant contributor to the overall response appeared to be the phosphorus moiety.

INTRODUCTION

A miniature glass bead containing rubidium silicate or oxide has been used in conjunction with a flame ionization detector for the analysis of nitrogen and phosphorus compounds[1,2]. This detector has several advantages over previously designed thermionic detectors, the main one being constant detector sensitivity by precise control of the electrical heating current.

The detector can be operated in two distinct modes: the phosphorus-mode (P mode)[2,3] and the nitrogen-phosphorus mode (N-P mode)[2,3]. These modes differ in that the P mode uses relatively high hydrogen flow-rates (20–35 *vs.* 2–4 ml/min) and air flow-rates (100–300 *vs.* 60–70 ml/min), but smaller electrical heating currents (2.0–2.4 *vs.* 2.6–3.6 A). In addition, the P mode has a zero flame-jet potential while in the N-P mode the potential is negative. A recent study of the detector in the N-P mode of operation, using azobenzene as a model compound, showed a close interrelationship between bead current and detector sensitivity[4]. For that reason, in the present study, we have performed parallel experiments in the P mode of operation

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using malathion and azobenzene as model compounds. The effects upon detector response of such variables as electrical heating current, hydrogen, carrier and air flows were investigated. Since the P mode showed an unexpectedly high sensitivity towards a nitrogen-containing compound, azobenzene, a comparative study of the sensitivities of azobenzene and malathion was also made. Whenever possible, the relative merits of operating in each mode will be presented.

EXPERIMENTAL

Chemicals

     Malathion, S(1,2-Dicarboxyethyl)-O,O-dimethyldithiophosphate, was obtained from the American Cyanamid Co. (Princeton, N.J., U.S.A.). Its purity was 99.3%. Azobenzene, reagent grade, was obtained from Eastman Organic Chemicals (Rochester, N.Y., U.S.A.). Each was dissolved in *n*-hexane (Nanograde, Mallinkrodt, St. Louis, Mo., U.S.A.), and two solutions were prepared containing 50 ng/μl and 5 ng/μl, respectively. The following insecticides were also used: diazinon [O,O-diethyl, O-(-isopropyl-O-6-methyl-4-pyrimidinyl)phosphorothioate]; methyl parathion (O,O-dimethyl, O-p-nitrophenyl phosphorothioate); and dursban (O,O-diethyl, O-3,5,6-trichloro-2-pyridyl)phosphorothioate. Solutions of these compounds containing 1–5 ng/μl were prepared in *n*-hexane.

     The hydrogen, air and nitrogen carrier gas (Selox, Inc.) were purified by passage through cartridges containing silica gel and molecular sieve 5A.

Apparatus

     The detector employed in this study was a Perkin–Elmer nitrogen-phosphorus detector mounted on a Perkin–Elmer Model 3920 gas chromatograph. A flame ionization detector, mounted in parallel with the nitrogen-phosphorus detector, received 48.5% of the injected sample. For certain experiments, the flame ionization detector was removed.

     The 0–5 mV output of the electrometer was fed into an instrumentation amplifier Model 610L (Analog Devices, Norwood, Mass., U.S.A.). That signal was digitized by using an Anscan Model 3700 (Beckman, Fullerton, Calif., U.S.A.) auto-ranging analog-to-digital converter. A PDP-11/20 computer (Digital Equipment Co., Manynard, Mass., U.S.A.) programmed in real-time BASIC was used to determine peak areas.

Procedures

     A glass column, 183 cm × 2 mm I.D., containing 3% OV-1 on 90–100 mesh Gas-Chrom Q (Applied Science Labs., State College, Pa., U.S.A.) was used. The injector was maintained at 260°, the column at 190° and the detectors at 260°. The column flow-rate was 80 ml/min except in those studies where it was varied.

     Samples were injected using a Hamilton No. 75 N 5-μl syringe (Supelco, Bellefonte, Pa., U.S.A.). The areas were obtained from the mean of two injections except in those experiments where noted. The sensitivities have been expressed either as coulombs per gram (C/g) or coulombs per mole (C/mole).

     In a previous study, a "bead current" was measured by recording the detector current in the N-P mode when no solute was passing through the detector block[4].

However, it was more difficult in the P mode to measure a bead current than in the N-P mode. In the P mode the flame-jet was grounded so that the negative potential of the bead, relative to the collector electrode, served to shield the collector from electrons generated in the flame[2,3]. Therefore, the bead current in this mode was usually very small (*i.e.*, <10 pA). Those small currents prevailed even under conditions of high bead temperatures and/or high rates of volatilization of alkali ions. It was possible, however, to measure a current by momentarily applying a negative polarity to the flame-jet. The resulting current is referred to as a bead current throughout this paper.

RESULTS

Effects of flow-rates of hydrogen and air on sensitivity

Since the solute ionization process was expected to be a function of the physical properties of the flame, the effects of hydrogen and air flow-rates were studied. Fig. 1 shows that the effects of the changes in flow-rates of hydrogen and air upon the bead current were quite different. As the hydrogen flow-rate was increased between 23 and 30 ml/min, a nearly linear change in bead current was displayed while at flow-rates greater than 30 ml/min the bead current increased exponentially. Fig. 2 shows that the sensitivity for malathion increased from 0.02 C/g–0.18 C/g, a factor of seven, as the hydrogen flow-rate was increased 12.7 ml/min. Meanwhile, the sensitivity of azobenzene remained essentially unchanged with increased hydrogen flow. Hence, a high flow-rate for hydrogen favored not only the sensitivity toward phosphorous but also the selectivity toward phosphorous, expressed as the sensitivity ratio of malathion/azobenzene. This implies that the mechanism of the detection was different for phosphorus than it was for nitrogen.

Increases of air flow-rates, between 100–200 ml/min, produced a slight increase in bead current as shown in Fig. 1. The increased production of a bead current was attributed to the increased rate of introduction of impurities by the air. Further
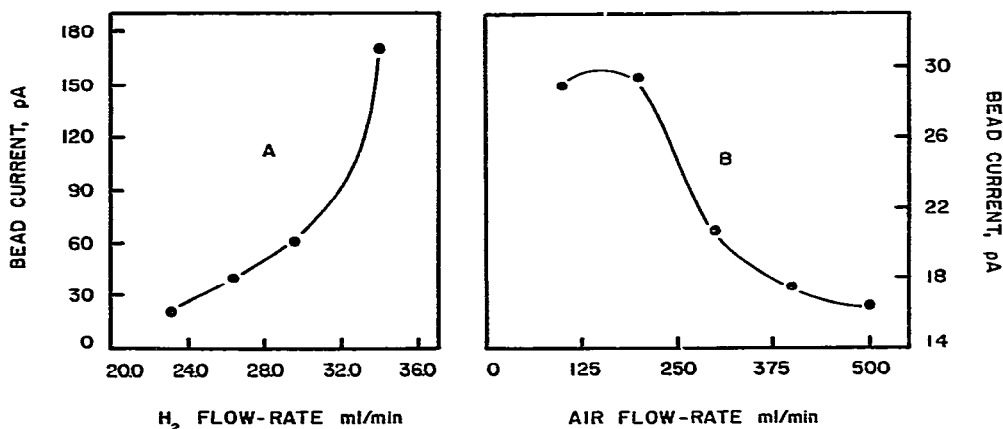

Fig. 1. Bead current in the P mode as a function of the flow-rate of hydrogen (A) and air (B). Carrier-gas flow-rate, 80 ml/min; heating current 2.15 A; air flow-rate, 100 ml/min (A), hydrogen flow-rate, (B), 30 ml/min.
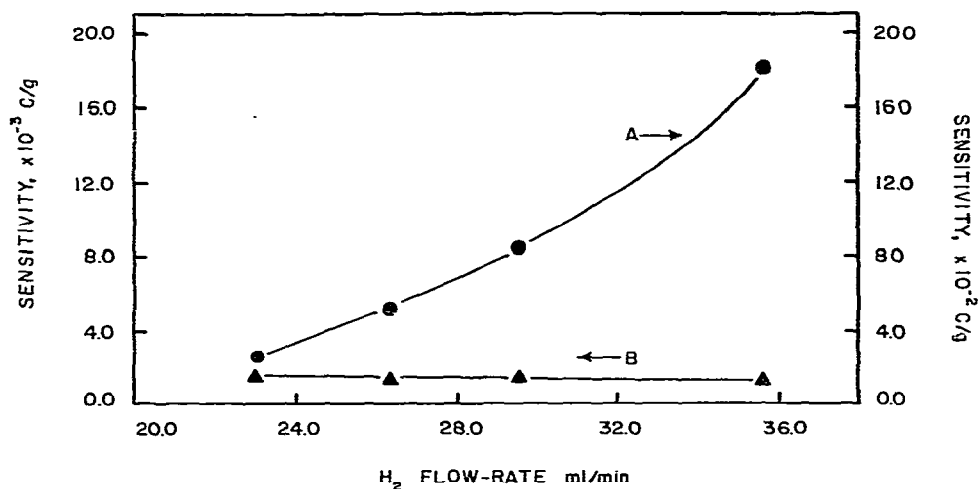
Fig. 2. Sensitivity in the P mode as a function of the hydrogen flow-rate. A = malathion; B = azobenzene. Heating current 2.15 A; carrier-gas flow-rate, 80 ml/min; air flow, 100 ml/min.

increases of air caused the bead current to decrease so that at 500 ml/min, the bead current was about one-half that at 200 ml/min. The decrease in bead current is thought to result from cooling of the bead and/or dilution of the hydrogen.

The effect of air upon sensitivity is shown in Fig. 3. For both malathion and azobenzene, the sensitivity remained approximately constant in the region of 100–200 ml/min of air with a subsequent decrease in the range of 200–500 ml/min. Meanwhile,
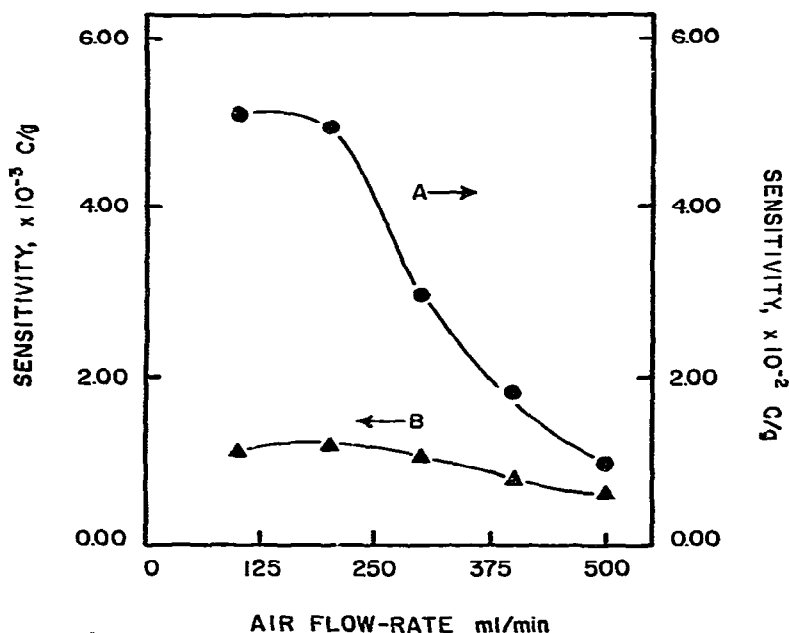

Fig. 3. Sensitivity in the P mode as a function of air flow-rate. A = malathion; B = azobenzene. Heating current 2.15 A; carrier-gas flow-rate 80 ml/min; hydrogen flow-rate, 30 ml/min.

the selectivity toward phosphorus decreased steadily as the flow-rate of air increased, ranging from a value of 43 at 200 ml/min to 17 at 500 ml/min. Thus, the changes in sensitivity roughly paralleled the changes of bead current. As a result, both sensitivity and selectivity toward phosphorus were favored by low flow-rates of air.

Effects of electrical heating on sensitivity

In the P mode, it is customary to operate with no electrical heating current so that the only contributor to bead temperature is the hydrogen flame[2,7]. However, Fig. 4 shows that favorable increases in sensitivity for both malathion and azobenzene could be obtained by utilizing electrical heating currents between 2.0 and 2.6 A. Electrical heating currents higher than 2.6 A were not used for fear of irreversible damage to the bead[4]. The exponential increases in the sensitivities reported may have been due to the exponential dependence of the vapor pressure of the alkali ions upon temperature.

Effect of bead current on sensitivity

For both malathion and azobenzene, the ratio of sensitivity to bead current was calculated and found to be constant. In other words, any change in sensitivity
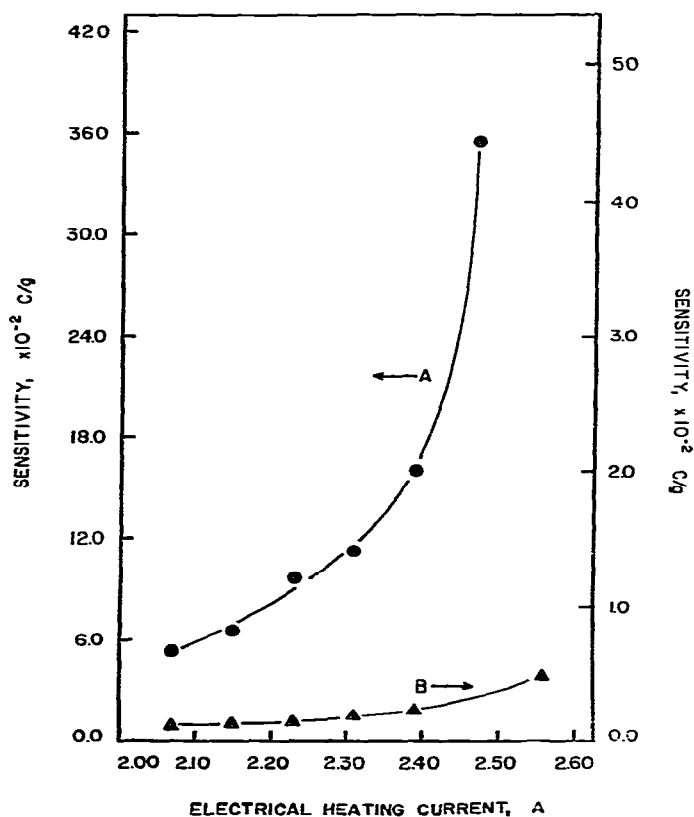

Fig. 4. Sensitivity in the P mode as a function of the heating current. A = malathion; B = azobenzene. Carrier-gas flow-rate, 80 ml/min; hydrogen flow-rate, 30 ml/min; air flow-rate, 100 ml/min.

resulting from a change in hydrogen flow, air flow, or heating current produced a proportional change in bead current. For malathion, changes in air flow-rate produced the greatest change in sensitivity per pA of bead current (2.85×10^{-3} C/g per pA), followed by electrical heating current (2.12×10^{-3} C/g per pA) and then hydrogen flow (1.33×10^{-3} C/g per pA). Azobenzene, however, showed a different trend. Electrical heating current had the largest effect (4.27×10^{-5} C/g per pA) followed by changes in air flow (3.22×10^{-5} C/g per pA). Hydrogen flow, as mentioned earlier, had no effect upon the sensitivity of azobenzene in the P mode.

Effect of carrier-gas flow-rate on sensitivity

Since carrier-gas flow-rate is often an important variable in a separation, its effect upon the response for malathion was studied. Because azobenzene would often overlap the solvent peak, it was not incorporated in the first part of the carrier-gas flow-rate study. Fig. 5 shows that the sensitivity for malathion increased slowly for flows from 25 to 40 ml/min, more rapidly above 40 ml/min, and then appeared to level off at flow-rates above 60 ml/min. Note the anomalous behavior in that the sensitivity increased as the bead current decreased.
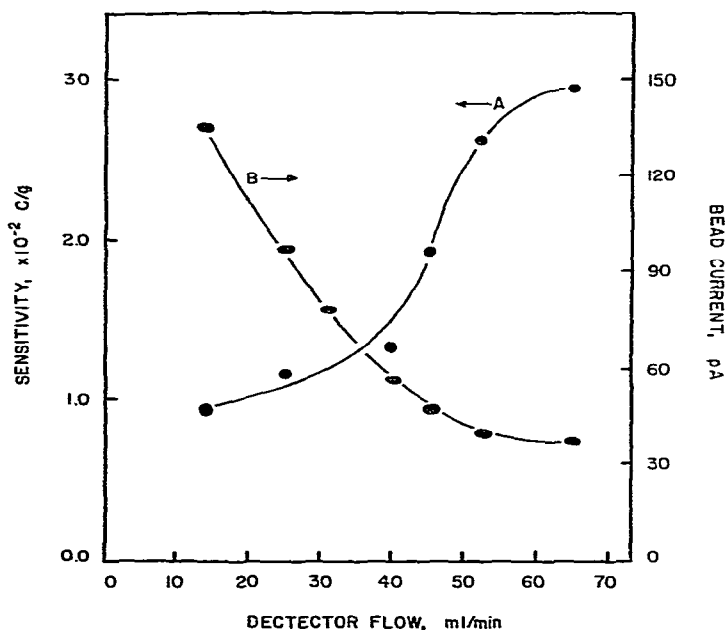

Fig. 5. Sensitivity for malathion and bead current in the P mode as a function of carrier-gas flow-rate. Heating current, 2.15 A; air flow-rate, 300 ml/min; hydrogen flow-rate, 28 ml/min.

In order to remove column effects from the study, an additional experiment was carried out in which the column flow was held constant at a low value, which would adequately resolve the solutes and the solvent, while additional carrier-gas was added at the column outlet. Fig. 6 shows that the sensitivities for both azobenzene and malathion reached a sharp maximum around 70 ml/min of total carrier-gas flow through the detector. Because the maximum sensitivity toward each compound
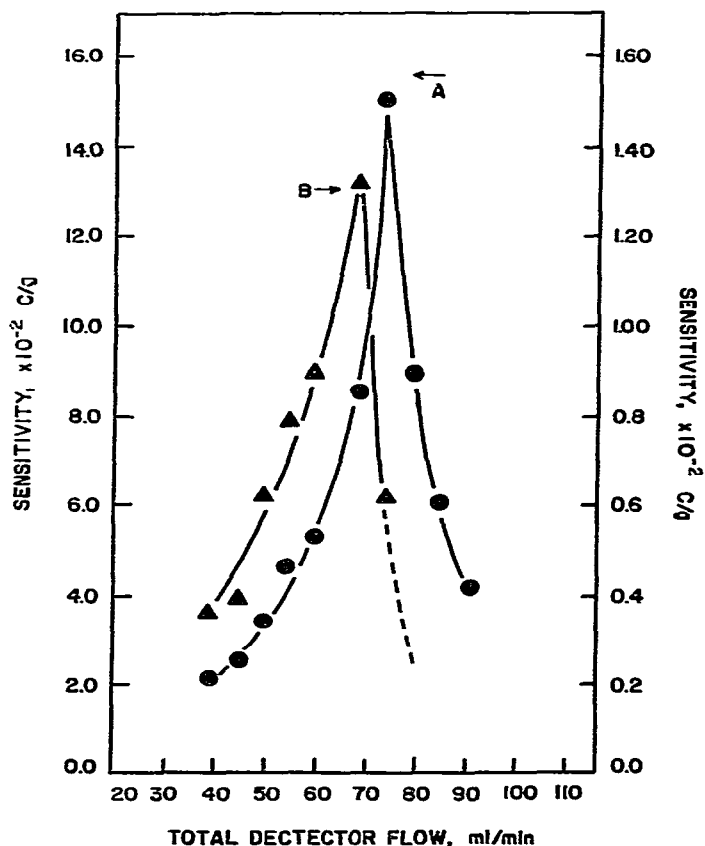
Fig. 6. Sensitivity in the P mode as a function of total carrier-gas flow through the detector. A = malathion; B = azobenzene. Heating current, 2.15 A; hydrogen flow-rate, 30 ml/min; air flow-rate, 300 ml/min; column flow-rate, 62 ml/min.

occurred at slightly different total flows, 68 ml/min for azobenzene and 74 ml/min for malathion, the selectivity for phosphorus changed drastically near 70 ml/min. Hence, at 74 ml/min, the selectivity toward malathion with respect to azobenzene was 4 times that of a flow-rate only 6 ml/min smaller.

Again, the sensitivity changes did not parallel those in the bead current. The latter decreased continuously with an increase in flow-rate.

Studies of signal-to-noise ratio

While changes in parameter settings often increased sensitivity, they sometimes disproportionately increased detector noise. Therefore, optimal settings were not necessarily found under conditions that gave maximal sensitivity. The signal-to-noise (S/N) ratios were obtained by measuring the respective currents for the peak height and the noise. Table I shows that an electrical heating current of 2.11 A, an air flow-rate of 500 ml/min, and a hydrogen flow-rate of 23.0 ml/min yielded the highest S/N ratio for malathion. Changing the heating current in either direction caused the ratio to decrease. Decreasing the hydrogen flow-rate also decreased the ratio. For azo-

TABLE I

STUDIES OF SIGNAL-TO-NOISE RATIOS AS A FUNCTION OF HEATING CURRENT AND GAS FLOWS

Heating current (A)	Air flow-rate (ml/min)	Hydrogen flow-rate (ml/min)	Noise (pA)	S/N ratio*	
				Azobenzene	Malathion
2.00	300	23.0	0.18	108	201
2.23	300	23.0	0.16	302	450
2.11	300	23.0	0.06	363	788
2.11	500	23.0	0.02	163	2500
2.11	300	17.5	0.03	81	683
2.11	200	23.0	0.28	85	302

* Average of duplicate injections of 8.03 ng of each compound.

benzene, the optimal S/N ratio differed in that it occurred at a lower flow-rate (300 ml/min) of air. Thus, the optimal air flow-rates were different from those that yielded higher sensitivities or specificities.

Reproducibility of response

This detector system has been shown to change sensitivity when operated in the N-P mode over a period of hours[4]. To determine if the conditions of the P mode were similar, a reproducibility study was performed by injecting malathion over a period of 7 h. From the data in Table II, it is evident that the response did not change significantly between 2.7 and 7 h, whereas the areas obtained using the N-P mode continued to decrease with time. A statistical F-test of the areas for the P mode showed that, at the 99% confidence interval, they were not significantly different. The slightly larger areas obtained at time zero were probably a result of not allowing sufficient time for the detector to stabilize after start-up. At least 1 h was found to be necessary in this mode of operation to obtain detector stability.

Sensitivities of the P mode toward selected insecticides

The sensitivities of the insecticides methyl-parathion, diazinon, and dursban were studied. All three contained both phosphorus and nitrogen, but methyl-parathion and dursban each contained one phosphorus and one nitrogen per molecule while

TABLE II

REPRODUCIBILITIES AND EFFECTS OF TIME ON THE RESPONSE

Time elapsed elapsed (h)	N-P mode*			P mode*		
	Bead current (pA)	Peak area (arb. units)	R.S.D.** (%)	Bead current (pA)	Peak area (arb. units)	R.S.D.** (%)
0	2.67	847.8	± 3.9%	45.4	412.9	± 1.3%
2.7	1.59	780.0	± 3.1%	48.6	338.6	± 5.1%
5.0	1.22	627.4	± 4.3%	47.7	342.5	± 8.1%
7.0	1.10	563.2	± 2.5%	49.3	341.4	± 3.9%

* Malathion injections of 8.03 ng in quintuplicate.
** Relative standard deviation.

diazinon contained one phosphorus and two nitrogens per molecule. With regard to the phosphorus moiety, diazinon and dursban were the most similar each having two ethylether groups in contrast to the two methylether groups of methyl-parathion. The relative sensitivities for these compounds were 1.0 for methyl-parathion, 1.3 for diazinon and 1.4 for dursban. The large difference between methyl-parathion and the other two insecticides suggests that, for this case, detection was more dependent upon the type of phosphorus moiety than the number of nitrogen atoms present in the molecule.

Response differences relative to the N-P mode

The quantitative response of this system was different from bead to bead. In order to make a fair comparison, selected experiments were run in the N-P mode on the same detector bead. Two major differences were noted. The P mode sensitivity toward malathion was 20% of that of the N-P mode while for azobenzene the sensitivity was 6% of that of the N-P mode, when 20 pA was used for both modes.

DISCUSSION

Operation of the detector in the P mode permitted the analysis of phosphorus compounds. However, it also gave the unexpectedly high sensitivity of $2 \cdot 10^{-3}$ C/g for azobenzene. The response to azobenzene was large enough to be considered adequate for specific detection of nitrogen compounds (in the absence of phosphorus). Therefore, the P mode should not be considered to be a phosphorus-specific detector as has been suggested by other workers[2,7].

Control of the carrier-gas flow-rate was found to be important for both the sensitivity and selectivity of the model compounds. The data showed that effects of carrier-gas flow on the response of the detector were complex. First, the sensitivity maximum could prove to be a disadvantage in that it couples column efficiency to component selectivity. While there presently appears to be no convenient way to decouple these factors, proper choice of the remaining parameters could be used to attain the most favorable sensitivities. Second, on the basis of its behavior, the P mode could not be classified as either a concentration-sensitive or mass-sensitive detector[5]. This was substantially different from the concentration-sensitive behavior for this same detector when used in the N-P mode[4]. There are two possible explanations. First, the detector response in this mode may be a combination of a mass- and a concentration-sensitive device[6]. Second, it is possible that the sensitivity depended upon the flame shape around the bead, the flame shape being a function of the gas velocity.

The detector stability was found to be adequate over a period of at least 4 h (after 1–2 h of "warm-up"). Operation in the P mode thus has a distinct advantage over the N-P mode. Since bead current measurements suggested the P mode operated at higher temperatures than the N-P mode, the trend in detector stability is contrary to the statement that rapid decay in bead current and sensitivity occurs at high bead temperatures[4].

The aging process, which is not consistent with the self-regeneration mechanism of Kolb and Bischoff[2], has until now been difficult to explain. The stability resulting from the conditions used in the P mode allow a plausible explanation. The major aging process of the bead is probably not the expected gradual loss of alkali, but

rather a change in the properties of the platinum wire. It is known that a reducing flame will cause embrittlement and cracking in platinum ware[8]. Subsequent to our earlier study, we observed that extended operation in the N-P mode resulted in the platinum wire turning white and breaking. Since in the P mode the effluent and hydrogen were ignited at the flame-jet, they did not provide the reducing atmosphere present in the N-P mode.

The study of the selected insecticides provided some additional insight into the role of the heteroatom upon sensitivity. It is apparent that the relative sensitivities were dependent upon the constituents bonded to the phosphorus as well as on the total amount of phosphorus present. It is less clear as to what percent of the detector response resulted from the nitrogen atoms and their manner of bonding within the molecule. These results suggest that parallel behavior, which was not recognized at the time, may have occurred in our earlier study of the N-P mode[4].

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