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STUDY OF THE NITROGEN RESPONSE MODE OF THE THERMIONIC RUBIDIUM SILICATE DETECTOR

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SUMMARY

The thermionic nitrogen detector has been found to be a concentration-sensitive detector. Bead current *vs.* heating current curves are continuously shifted toward higher heating currents and bead life may be as short as two months. The bead current and sensitivity are strongly dependent on carrier gas, hydrogen, and air flow-rates. The optimum bead current compatible with minimal bead aging is 10-30 pA. Sensitivity changes obtained by increasing bead current due to increasing hydrogen flow-rates are larger than corresponding changes obtained by electrical heating. Optimum signal-to-noise ratios were obtained at a hydrogen flow-rate of 2-4 ml/min and an air flow-rate of 60-70 ml/min.

INTRODUCTION

A thermionic detector which utilizes a non-volatile rubidium silicate glass bead heated electrically has been recently described^{1,2}. The detector is capable of operating in the phosphorus or nitrogen-phosphorus mode. It was suggested by Kolb and Bischoff¹ that the relatively long life of the glass bead was due to the non-volatile character of the rubidium silicate in the bead and the fact that the generated rubidium ion is immediately recaptured by the bead. The detector bead current was shown to decrease when the carrier gas flow-rate increased by a factor of 1.75, while, at the same time, the sensitivity decreased by a factor of 2.

In this work, we studied the response of the nitrogen-phosphorus detection mode of the detector in a systematic fashion so as to observe the relationship of the bead current *vs.* sensitivity when the carrier gas flow-rate, air flow-rate, or hydrogen flow-rate was changed. Because detector noise increased exponentially when bead current increased due to deliberate changes of the previously mentioned variables, signal-to-noise ratio studies were made. The rubidium bead can age rather rapidly and the bead current decreases daily, thereby shifting the bead current *vs.* heating current relationship to higher heating currents.

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Most of the basic work was done using azobenzene, although the responses of a few selected nitrogen and phosphorus-containing insecticides were also determined, particularly as a function of hydrogen flow-rate. The detector has been shown to be concentration sensitive—an unusual characteristic for an ionization detector which utilizes auxiliary gases such as hydrogen and air in its detection mechanism³.

EXPERIMENTAL

Chemicals

Azobenzene (reagent grade; Eastman, Rochester, N.Y., U.S.A.) dissolved in *n*-hexane (reagent grade; J. T. Baker, Phillipsburg, N.J., U.S.A.) was used to prepare solutions from 0.05–1000 ng/ μ l. The following insecticides were used: diazinon (O,O-diethyl O-(2-isopropyl-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/ μ l were prepared in *n*-hexane. The injector was maintained at 200°, the column at 140°, and the detectors at 300°.

Nitrogen was used as the carrier gas and all gases were purified by passage through 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 was mounted in parallel with the nitrogen detector, and the column effluent was split so that 51.5% of the sample entered the nitrogen detector. The detector was also operated under conditions such that it could receive the total column flow.

The 0–9 V computer-compatible output of the electrometer was fed into a laboratory-made instrumentation amplifier which amplified the signal by a factor of 100. That signal was digitized by using an Anscan Model 3700 (Beckman, Fullerton, Calif., U.S.A.) auto-ranging analog-to-digital converter. The analog-to-digital converter was interfaced to a PDP-11/20 computer (Digital Equipment, Maynard, Mass., U.S.A.) which was programmed in real-time BASIC for area measurements.

Procedures

The glass column was 6 ft. \times 2 mm I.D. and contained 3% OV-1 on 80–100 mesh Gas-Chrom Q (Applied Science Labs., State College, Pa., U.S.A.). The sensitivity of the electrometer was 5×10^{-12} A for a full-scale deflection on its most sensitive range. The noise was measured as the peak-to-peak perturbation of the bead current over a short time period.

RESULTS AND DISCUSSION

Bead vs. heating current

Throughout this paper the current measured when no solute is passing through the column is called bead current. This current is primarily the result of the ionization process in the immediate vicinity of the bead due to the interaction of rubidium atoms

with hydrogen atoms¹. There are other possible minor contributions to this current which arise from column bleed, impurities in the carrier gas, hydrogen, and air. Thus, this is analogous to the standing current terminology employed in electron capture detectors.

The power supply which provides constant current to the bead was calibrated. The relationship between dial setting and heating current was not linear, as shown in Fig. 1, over the range of 2.0–3.6 A. At zero dial setting the current passing through the bed was 2.0 A. The latter is important to know because passage of the heating current causes a shift in the curves of the bead vs. heating currents to higher currents. It is advisable to disconnect the power supply to insure no passage of current when the detector is not used. This curve has also been included for the purpose of providing a means for comparing results of different workers in terms of the amperage used in heating, since the equipment required for calibrating these relatively high currents is not readily available to the practicing gas chromatographer.

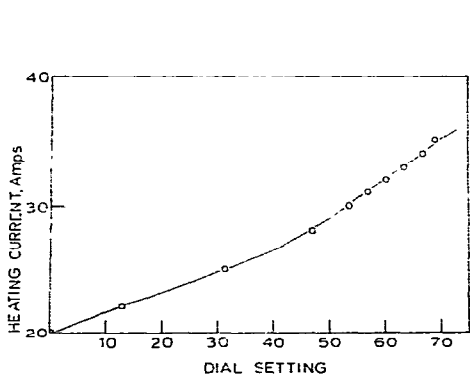


Fig. 1. Heating current as a function of dial setting.

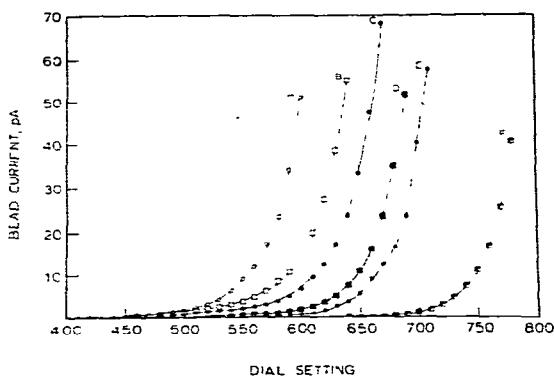


Fig. 2. Bead current as a function of dial setting and time elapsed from bead installation. A = Day 1; B = Day 4; C = Day 8; D = Day 11; E = Day 16; F = Day 20.

The bead vs. heating current relationship measured over a 20-day period is shown in Fig. 2. Linear changes in heating current in the range of 2.8–3.8 A resulted in an exponential change in the bead current. Thus, over a 16-day period, a new bead decreased its bead current from 51 to 0.8 pA. This is an important consideration in obtaining reproducibility and high sensitivity. Furthermore, since the power supply is designed to automatically shut off the heating current in the vicinity of 4.0–4.5 A, the bead is no longer usable if larger heating currents are necessary in order to attain 10–30 pA of bead current. This range of bead current is necessary to achieve the concomitant desired sensitivity, for reasons which will be discussed later.

The measurements of bead vs. heating current required the passage of high heating currents in order to attain the 50–70 pA of bead current which are the limiting values consistent with the noise and drift. These higher heating currents rapidly aged the bead and shifted the bead vs. heating current curve to yet higher heating currents. These observations indicate that a bead used at a suitable bead current may deteriorate in shorter periods of time than those predicted by Kolb and

Bischoff¹, a fact which is not consistent with a self-regeneration mechanism. Cleaning the detector did not reveal the presence of salt deposits as is the case with thermionic detectors employing volatile alkali salts.

It is also interesting to note that neither changes in carrier gas flow-rate, hydrogen flow-rate, nor air flow-rate altered the shape of the curves obtained in Fig. 2. Changes in these variables, however, sometimes altered the heating current required for the onset of a sustained ionization process which, in turn, permitted both a measurable bead current and the limiting usable bead current consistent with noise and drift to be attained.

Effect of carrier gas flow-rate upon bead current and sensitivity

The dependence of bead current on carrier gas flow-rate is shown in Fig. 3 for two different heating currents. Increasing the heating current by 60 mA did not alter the relationship between carrier gas flow-rate and bead current, but only changed the magnitude of the current. From 0.5–5 ml/min, the bead current increased to a maximum; from 5–120 ml/min, the current decreased as flow-rate increased. The increase at low flow-rates may have been due to response of the detector to bleed from the column. The increase ceased when the flow-rate became large enough to rapidly cool the bead by a thermal conductivity effect, thus overcoming any possible increase in bead current due to increases of column bleed. This is a possible consideration if the detector has a non-specific response to the silicone liquid phase.

Fig. 4 shows the simultaneous dependence of bead current and response

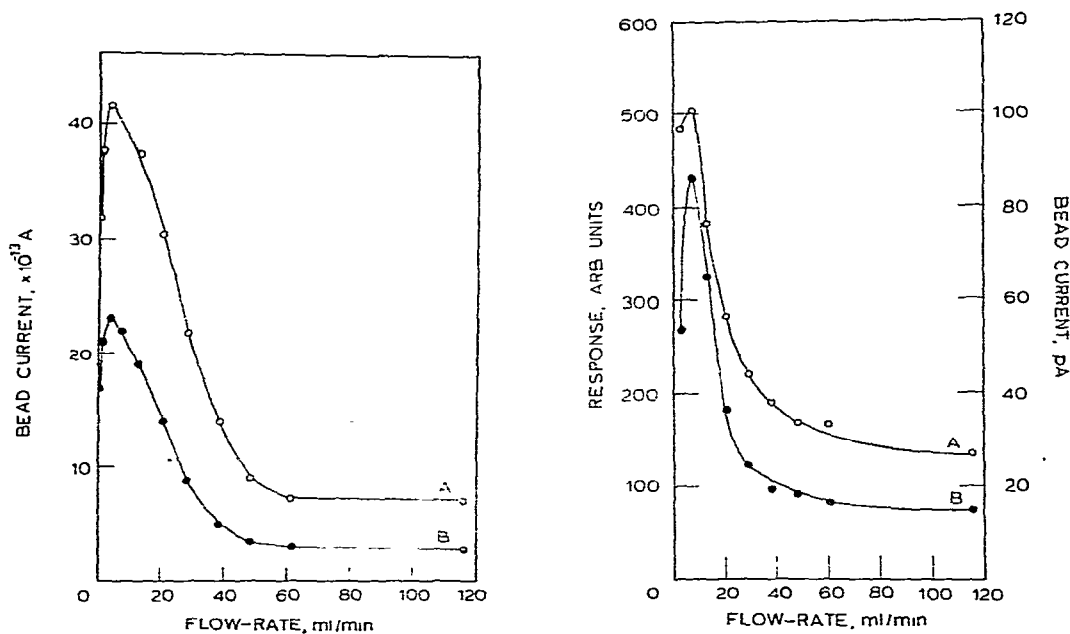


Fig. 3. Bead current as a function of carrier gas flow-rate. Hydrogen flow-rate, 2.50 ml/min; air flow-rate, 83.5 ml/min. A = 3.20 A heating current; B = 3.14 A heating current.

Fig. 4. Sensitivity (A) and bead current (B) as a function of carrier gas flow-rate. Azobenzene, 7.88 ng. Hydrogen flow-rate, 2.50 ml/min; air flow-rate, 83.5 ml/min.

(signal) as a function of carrier gas flow-rate. Except for flow-rates less than 7 ml/min, the detector met the Halasz⁴ criterion of a concentration-sensitive detector where the response is inversely proportional to the carrier gas flow-rate. It is also interesting to note that in the region of 1–7 ml/min, the response increased by 3% while the bead current almost doubled — a fact consistent with the explanation that the increases in bead current at these low flow-rates were due mainly to column bleed.

Previously designed thermionic detectors which depend on a flame temperature to volatilize the alkali salt have been found to be mass flow-sensitive detectors³. Although the design of the present detector has a flame tip for convenience in using the detector as a flame ionization detector, combustion of the air–hydrogen mixture takes place near the glowing filament, and a proper flame profile does not exist. Thus, as the flow-rate of carrier gas and/or air increases, heat is removed from the bead and the mass flow-rate of hydrogen is diluted; consequently, the bead current will decrease.

Effect of changes in heating current upon bead current and sensitivity

Since the heating current changed the bead current, it was of interest to determine the relationship between the sensitivity and the bead current. The sensitivity, expressed in terms of coulombs for a constant injection of 7.9 ng of azobenzene, as a function of bead current is shown in Fig. 5. The sensitivity increased linearly with bead current up to a value of 220 pA, beyond which the changes were not linear. Thus, it is important to note, with the aid of Fig. 2, that a seven-day operational period caused the bead current to decrease by a factor of about 5, which concomitantly

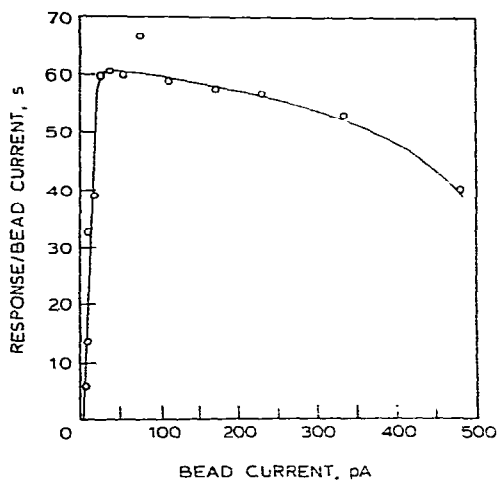
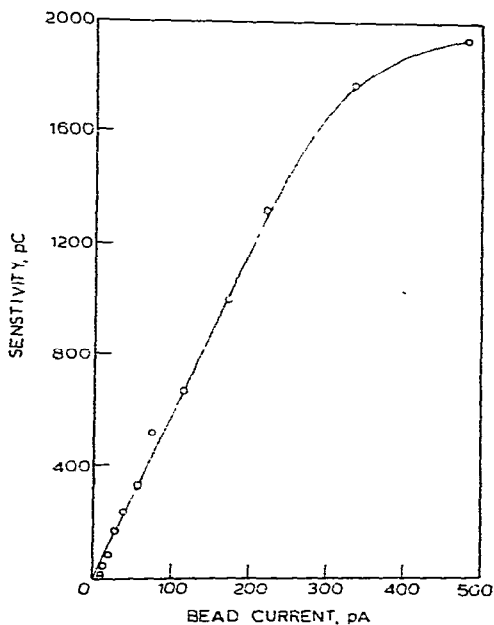


Fig. 5. Sensitivity as a function of bead current. Azobenzene, 7.88 ng. Hydrogen flow-rate, 2.50 ml/min; air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min.

Fig. 6. Response/bead current as a function of bead current. Azobenzene, 7.88 ng. Hydrogen flow-rate, 2.50 ml/min; air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min.

decreased the sensitivity by a similar value when the current varies within the linear range of Fig. 5.

It is evident from Fig. 5 that strict control of bead current was essential for obtaining signal reproducibility; thus, a change of 15 mA of heating current caused a change of 1 pA in the bead current. Table I shows that areas obtained over a seven-hour period had an overall relative standard deviation of 0.94%. However, hourly increases in heating current were required to maintain constant sensitivity during this period. Table I also shows that the response decreased rapidly within a 48-h period due to aging of the bead; that, in turn, caused a rapid decrease in bead current.

TABLE I
REPRODUCIBILITY STUDIES OF PEAK AREAS

<i>Time elapsed (h)</i>	<i>Heating current (dial setting)</i>	<i>Bead current (pA)</i>	<i>Area response* (arbitrary units)</i>
<i>A. Constant bead current</i>			
0	7.236	14.3	4622
1	7.242	14.3	4606
2	7.264	14.3	4718
3	7.278	14.3	4659
4	7.298	14.3	4690
5	7.320	14.3	4704
6	7.345	14.3	4705
		Av. 4672	
		R.S.D.***	0.94%
<i>B. Constant heating current</i>			
0**	6.600	14.3	7320
6	6.600	11.3	5823
24	6.600	7.20	3462
48	6.600	4.17	1685

* Constant azobenzene injection of 11.8 ng.

** Initial setting not changed over a period of 48 h.

*** R.S.D. = Relative standard deviation.

If the ratio of peak area (pA · sec) to bead current is plotted as a function of the bead current in pA, the relationship shown in Fig. 6 was obtained. The initial linear increase of this ratio ceased at about 30 pA of bead current following which the ratio slowly decreased. The significance of this plot lies in the fact that it indicates the efficiency of interaction between the alkali ions supplied by the bead and the ionic species responsible for specific detection. In the region of 0–30 pA, the product of pA and sec was up to six times larger than the bead current. Fig. 5 shows that increasing the heating current to generate a higher bead current magnified the response, but Fig. 6 shows that the response obtained per unit of energy consumed did not increase. Therefore, although the sensitivity shown in Fig. 5 increased beyond 30 pA, the efficiency, as measured by the ionization current obtained per unit of bead current, decreased slowly. Consequently, operation of the bead at heating currents above 30 pA of bead current yielded higher sensitivity in exchange for impractical use of the bead under conditions which resulted in more rapid aging.

Effect of changes in hydrogen flow-rate upon bead current and sensitivity

Increasing the hydrogen flow-rate from 1.8–9 ml/min increased the bead current as shown by curve B in Fig. 7. Both the bead current and the noise (curve A) increased exponentially. Note the similarity between these curves and the ones obtained by increasing the bead current by electrical heating of the bead. At flow-rates higher than 9 ml/min, higher noise and larger drift made detector operation difficult. The importance of strict hydrogen control is obvious, in the region 3–7 ml/min of hydrogen flow-rate, where the bead current changed by a factor of 30.

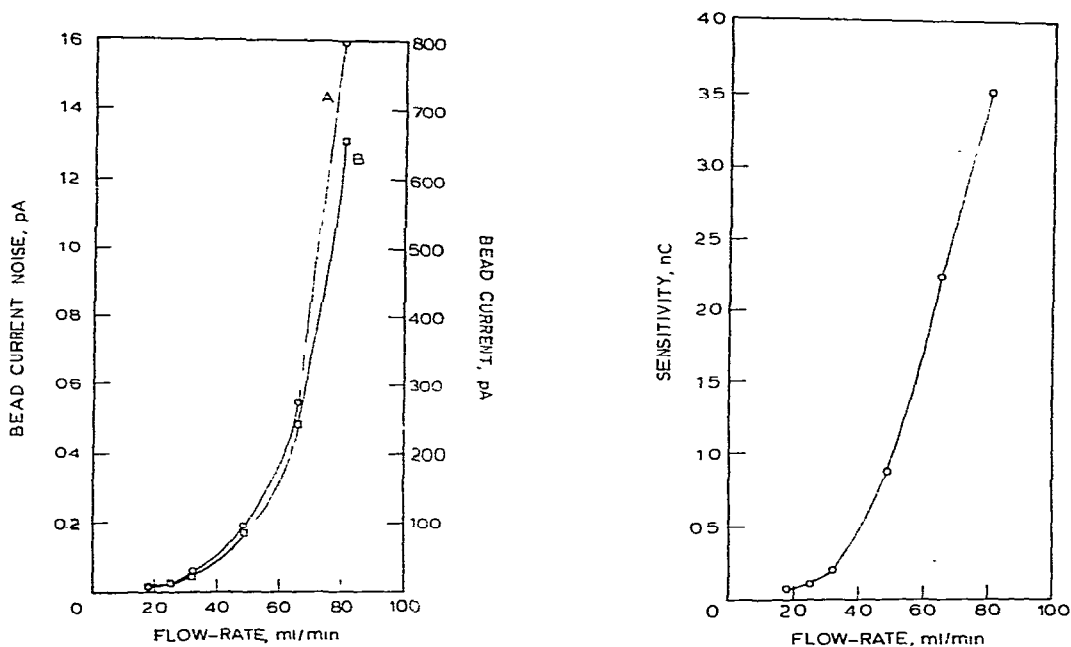


Fig. 7. Bead current noise (A) and bead current (B) as a function of hydrogen flow-rate. Air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min.

Fig. 8. Sensitivity as a function of hydrogen flow-rate. Azobenzene, 7.88 ng. Air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min.

It is also important to note that the sensitivity, expressed in coulombs for 7.9 ng of azobenzene, also changed exponentially, as shown in Fig. 8. Sensitivities of 2000–3000 pC were readily obtained and these are higher than those achieved by electrical heating (Fig. 5). When the data in Figs. 7 and 8 were replotted to show sensitivity as a function of bead current at different hydrogen flow-rates, the resulting curve was similar to that shown in Fig. 5; however, the slope of the linear portion was 10 pC/pA rather than 5.8 pC/pA. Thus, changes in hydrogen flow-rate had a more pronounced effect upon sensitivity than changes in heating current. To show this difference in sensitivity, azobenzene was injected at different hydrogen flow-rates, but the heating current was diminished so as to maintain constant bead currents of 7.58 pA and 28.06 pA. Fig. 9 shows that an increase in hydrogen flow-rate caused an increase in sensitivity at a constant bead current.

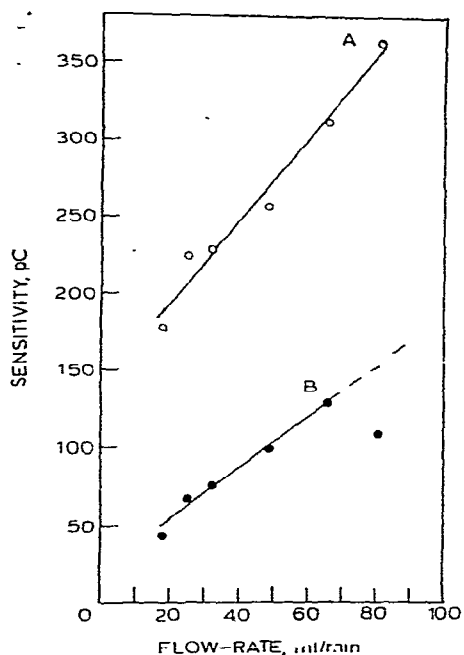


Fig. 9. Sensitivity as a function of hydrogen flow-rate at constant bead current. Azobenzene, 7.88 ng. Air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min. A = 28.06 pA bead current; B = 7.58 pA bead current.

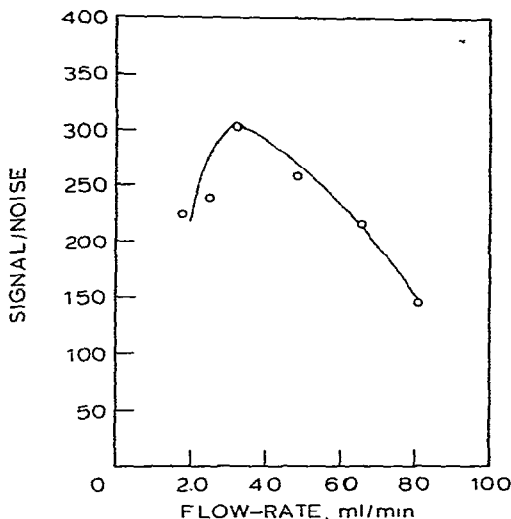


Fig. 10. Signal-to-noise ratio as a function of hydrogen flow-rate. Azobenzene, 7.88 ng. Air flow-rate, 83.5 ml/min; carrier gas flow-rate, 38.0 ml/min.

This result suggests that an increase in the hydrogen atom concentration around the bead yields a higher concentration of vaporized alkali atoms than the one obtained by heating. A more practical implication is the fact that a change in the electrical heating of the bead can be used to compensate for a change in bead current due to effects such as aging. If, however, changes in the hydrogen flow-rate should occur, maintaining the bead current constant will not maintain constant sensitivity. Therefore, an inability to maintain constant sensitivity may indicate a problem with controlling the hydrogen flow-rate.

These results show the opposite behavior to those obtained in a similar study performed by Kolb and Bischoff¹ which showed that increases in hydrogen flow-rate decreased the sensitivity of pyridine at constant bead current. For that reason, the effect of flow-rate on sensitivity at a bead current of 7.20 pA was tested using a mixture of three insecticides: diazinon, methyl parathion, and dursban. The results in Table II confirm the increase in sensitivity with increasing flow-rate at constant bead current.

In addition, we observed differences in the absolute responses (C/mole) among the three insecticides and azobenzene. The insecticides exhibited much higher responses than azobenzene, which had a sensitivity in the range of 1-3 C/mole under similar conditions. It can also be noted that, although diazinon contains two heterocyclic nitrogen atoms and dursban only one, the response of the two compounds was almost identical at all flow-rates. The methyl parathion, however, which contains only

TABLE II

EFFECT OF HYDROGEN FLOW-RATE UPON THE RESPONSE OF SELECTED INSECTICIDES

Hydrogen flow-rate (ml/min)**	Response* (C/mole)		
	Diazinon	Methyl parathion	Dursban
1.78	48	24	47
3.21	90	53	91
4.86	142	96	143
6.59	155	103	154
8.08	130	94	131

* Response reproducibility of duplicates was generally within ± 1 .

** Bead current constant at 7.28 pA.

one nitrogen (in a nitro-group), exhibited a distinctly lower sensitivity than either of the other pesticides, but still a much higher one than the azobenzene. There is a definite need, therefore, for more comparative studies of this type for a variety of nitrogen-containing compounds, particularly those containing phosphorus and other hetero atoms.

Fig. 7 showed that as the hydrogen flow-rate increased the noise of the bead current also increased exponentially. Thus, it is important for establishing optimal conditions that the signal-to-noise ratio be considered when increasing the bead current by increasing the hydrogen flow. The relationship obtained for a constant injection of 7.9 ng of azobenzene (Fig. 10) shows that a maximum was obtained at a flow-rate of 3.2 ml/min. Therefore, the hydrogen should be operated in the range of 2.5–4.5 ml/min. The relatively lower signal-to-noise ratio obtained in the region of 6–7 ml/min may account for the large deviations from linearity in the sensitivity measurements at 7.58 pA shown in Fig. 9.

Effect of changes in air flow-rate upon bead current and sensitivity

The change in bead current and noise as a function of the air flow-rate is shown in Fig. 11. The overall effect is similar to the one observed for the carrier gas. A flow-rate of air of 13 ml/min was the minimum that could be used to obtain a relatively stable bead current. As the flow-rate was increased, the bead current reached a maximum at 24.5 ml/min (which may be due to combustion of impurities in the air) and then decreased due to both cooling of the bead by the air and dilution of the hydrogen. The change in the noise was very similar to that of the bead current. The sensitivity, expressed in coulombs, for constant injections of azobenzene is shown in Fig. 12 as a function of air flow-rate. As in all our studies of other variables that affect the bead current, the results show that changes in sensitivity paralleled those of bead current. From the data in Figs. 11 and 12, one can plot the sensitivity as a function of the resulting bead current as the air flow-rate is changed. This resulted in a straight line having a slope of 9.83 pC/pA. Since this value is different from that obtained by changing the sensitivity in terms of heating current, and since the air flow-rate-sensitivity relationship changed with age of the bead, one cannot correct for a change in sensitivity due to a change in air flow-rate by electrically heating the bead.

Although the sensitivity was at a maximum near 25 ml/min, Fig. 13 shows that

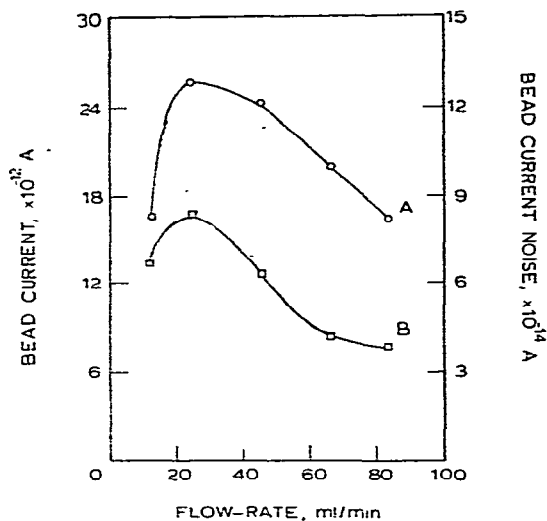


Fig. 11. Bead current (A) and bead current noise (B) as a function of air flow-rate. Hydrogen flow-rate, 2.50 ml/min; carrier gas flow-rate, 38.0 ml/min.

the signal-to-noise ratio reached a maximum at 68 ml/min. Unfortunately, the majority of the studies in this paper were done at an air flow-rate of 83 ml/min, because this value was recommended as the optimum⁵. Clearly, users of this detector should check the performance of each bead because that value may be different for each.

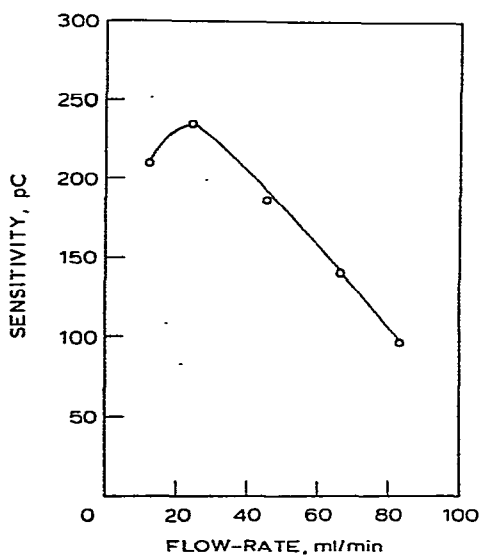


Fig. 12. Sensitivity as a function of air flow-rate. Azobenzene, 7.88 ng. Hydrogen flow-rate, 2.50 ml/min; carrier gas flow-rate, 38.0 ml/min.

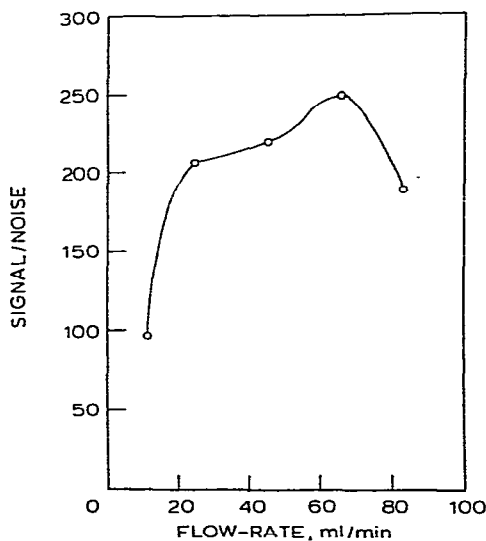


Fig. 13. Signal-to-noise ratio as a function of air flow-rate. Azobenzene, 7.88 ng. Hydrogen flow-rate, 2.50 ml/min; carrier gas flow-rate, 38.0 ml/min.

The linear range of the detector was determined using azobenzene in *n*-hexane by plotting the response/sample weight *versus* log of the sample weight. The range was 10^4 , from 10^{-10} – 10^{-6} g, and agrees well with a linearity study performed under different operational conditions². Thus the linear range was not extensively studied.

CONCLUSIONS

Control of all the variables that affect the background current is essential to attain constant sensitivity. The main advantage of this detector from previously commercially available thermionic detectors lies in the fact that aging or alkali volatilization can be compensated for, up to a point, by continuously increasing the heating current. However, it is not conveniently possible to compensate electrically for changes in bead current due to variations in the flow-rates of hydrogen, air, or carrier gas. Thus, particular care must be taken in their regulation to obtain reproducible results. It should also be noted that our results show the optimal hydrogen flow-rate to be in the range of 2.5–4.5 ml/min, and that lower flow-rates at constant bead current will not increase sensitivity, as previously indicated¹.

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