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OPTIMISATION OF THE PERFORMANCE OF A THREE-ELECTRODE THERMIONIC DETECTOR FOR THE DETECTION OF PHOSPHORUS, SULPHUR AND NITROGEN COMPOUNDS BY GAS CHROMATOGRAPHY

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SUMMARY

The main operating parameters and the performance of a commercial thermionic detector have been investigated. The variation of response to phosphorus-, sulphur- and nitrogen-containing compounds is recorded as a function of the position of the electrode assembly for a wide variety of flame conditions. The maximum sensitivities obtainable with the detector are compared with those of the flame ionisation detector (FID). It is shown that the detector may be operated in various modes to improve the simplicity of operation for routine use, to obtain selective responses individually for each type of compound or to give equal response to P-, S- and N-containing compounds while discriminating against hydrocarbons. The recommended conditions for obtaining the various operating modes are summarized and suggestions are made as to the best way of reliably setting-up the detector and using it for routine analysis. Although the detector's sensitivity is by far the greatest for P-compounds, its utility as a selective detector for either S- or N-compounds is also apparent.

INTRODUCTION

The alkali flame ionisation detector (AFID) or thermionic detector (TD) has appeared in several forms since it was first described by Karmen and Giuffrida[1] in 1964 and has been the subject of numerous published studies of varying complexity[2–8]. Nevertheless, there still remains some doubt as to the type of response obtained from each detector design, the way in which performance can vary with operating conditions and whether or not particular designs give a sufficiently stable and reproducible response for routine gas chromatography.

An investigation has been made into the performance of a commercial, three-electrode detector[9] in which the alkali metal salt is mounted in a negatively charged cylinder held just above the jet, while the jet and a central collector electrode are earthed. The effect of various operating parameters on the response of the detector to compounds containing P, N or S atoms is reported. It is shown that even with a single detector design several different modes of operation can be identified and that it may be necessary to sacrifice some of the inherent sensitivity or selectivity of the detector in return for simple and reliable routine use.

EXPERIMENTAL

Apparatus

The work was carried out using a Pye 104 gas chromatograph fitted with dual FID–thermionic detectors mounted in a temperature stabilised oven. The TD is a standard Pye design supplied as a "nitrogen-selective" detector by using a larger jet aperture and rubidium chloride as the alkali metal salt[10]. The collector electrode and the rubidium chloride crystal and its holder are arranged as a central probe assembly, the performance of the detector being varied by changing the height of this probe relative to the jet. To facilitate the large number of measurements required, a micrometer attachment was fitted to the probe so that its height could be rapidly set to any required value. For routine work, washers of known thickness were used to ensure reproducible settings of the height. The standard gas controls were used for the FID but it was found essential to use precision regulators and gauges for the TD. The equipment used (summarized in Table I) allowed the air and hydrogen flow-rates to be maintained within limits of 0.1 and 0.02 ml/min, respectively. The auxiliary nitrogen flow was supplied to the detector by a connection to the column outlet, allowing the total nitrogen flow through the detector to be increased while maintaining the carrier gas flow constant at 25 ml/min. All measurements were made using 1.5 m × 4 mm I.D. glass columns packed with 5% OV-17 on Gas-Chrom Q.

The rubidium chloride crystal and its holder (a perforated, cylindrical electrode concentric with the detector body and the central collector electrode) were maintained at −170 V. Signals on the collector electrode were measured with a Pye wide-range amplifier giving a maximum sensitivity of 1×10^{-12} A f.s.d. when used in conjunction with a 10-mV chart recorder. The detector was modified to provide rigid clamping of

TABLE I

GAS CONTROLS USED WITH THERMIONIC DETECTOR

Gas	*Type of regulation*	*Range of flow-rate (ml/min)*	*Regulator*	*Gauge*
Nitrogen to column	Constant flow controller	0–60	Brookes, type 8744A	None
Auxiliary nitrogen	Fixed orifice and constant pressure regulator	0–60	Manostat, type 10A	Budenburg, 3-in. Simplex gauge, 0–30 p.s.i.
Air	Fixed orifice and constant pressure regulator	0–550	Manostat, type 10A with multi-turn control spindle	Budenburg, 4-in. bronze tube gauge 3–15 p.s.i.
Hydrogen	Fixed orifice and constant pressure regulator	0–60	Brookes, type 8601	Budenburg, 10-in. standard test gauge, 0–20 p.s.i.

the connecting cable at the point of entry; with the original design it was found that any movement of the cable caused slight movement of the collector electrode and considerably increased the noise level of the detector. This modification resulted in excellent noise levels without the need to resort to additional damping of the recorder signal.

Performance studies

The total number of variable parameters with this type of detector is large. It includes the nitrogen, air and hydrogen flows, the height of the collector electrode above the flame, the position and shape of the alkali crystal relative to the collector and the flame, the polarizing voltage applied to the crystal, the temperature of the detector oven, and the type of alkali salt used. In order to reduce the complexity of the task several of the parameters were fixed, the selection being based on experience with the use of the detector as well as on practical limitations. Thus only RbCl crystals were used, although CsBr is also available from Pye and other salts can be pressed into suitable holders without difficulty. The detector oven was maintained at 350° (the maximum usable without overheating the coaxial lead to the collector); lower temperatures simply reduce the background current obtained with a given set of conditions. The polarising voltage was kept constant as it produces only small changes in response provided the field strength is sufficient to ensure proper collection of ions.

The geometry of the detector (*i.e.*, the position of the electrodes and crystal relative to the flame) is of considerable importance. However, the design of the Pye detector makes it difficult to observe the effects of each parameter unambiguously, the effects of the detector geometry being closely linked to the flame conditions since changes of gas flow vary not only the flame composition and temperature but also its size and shape. The height of the central collector electrode is a critical parameter, as at least part of the selectivity of the thermionic detector is thought to arise from differences in the lifetimes of the ions formed by different heteroatoms. That is, these ions persist to different heights in and above the flame so that a change of collector electrode height can vary the relative responses of different heteroatoms. With the Pye design, variation of the collector height by movement of the central probe simultaneously changes the position of the RbCl crystal. It is possible to avoid this by repositioning the crystal in the holder but this is laborious and difficult to carry out accurately. Movement of the crystal has two possible effects; the most important is the change in rate of vaporisation of RbCl (*i.e.*, a change in background current) as the temperature of the crystal surface varies. A second effect may occur with the Pye design because a negative potential is applied to the crystal to remove unwanted ions (*e.g.*, hydrocarbon ions formed by a normal FID mechanism) before they reach the collector electrode. Thus, movement of the crystal assembly may alter the response of the detector to "unwanted" compounds such as hydrocarbon solvents, even though there should be no direct effect due to the change in background current.

Experience with the detector suggests that an increase of background current increases the sensitivity of the detector to those heteroatoms responding through the thermionic mechanism, but has little effect on their relative response. In normal use, the maximum usable value of the background current is governed by the increases of signal noise and of background drift as the crystal burns away more rapidly. For most of the experiments described here it was decided to locate the crystal in its holder so that a usable background current was obtained over a reasonable range of probe heights, allowing the effect of changes in collector height to be observed. The best location was found to be where the tip of the jet is level with the lower rim of the crystal when the central probe is at its lowest position. This setting gives the minimum separation of the flame and the collector electrode, the end of the collector then being 8.5 mm above the tip of the jet. Thus, this figure should be added to the probe heights given in the results in order to obtain the true height of the collector.

As mentioned above, changes in the gas flow-rates vary the dimensions of the flame. Thus the effect of a change in flame conditions will also depend on the position of the probe assembly. It was therefore decided to base the main study of the detector's parameters on plots of the effect of probe height on background signal and response under different flame conditions. The sets of flame conditions were chosen so as to illustrate the effects of air flow-rate, of the total hydrogen plus nitrogen flow-rate through the jet, and of the hydrogen to nitrogen ratio. In order to carry out these measurements it was necessary not only to decide on the best compromise for the position of the RbCl crystal in its holder (see above), but also the way in which it should be "conditioned" to the flame shape. As RbCl is vaporised during operation, a new crystal tends to lose RbCl until its inner surface has assumed the shape of the flame, when it settles down to a steady background current with low loss of RbCl. Any change in the flame conditions or probe height which produces a large increase in background signal will therefore irreversibly alter the shape of the crystal. Conditioning of the crystal was standardised by using the following procedure:

(1) Set the crystal in the probe assembly so that its metal holder protrudes 11.5 mm and check the parallel alignment of crystal, collector and probe assembly.

(2) Light the flame with gas flow-rates of air 100, nitrogen 30, and hydrogen 30 ml/min. Push the probe assembly hard down into the detector body taking care not to extinguish the flame.

(3) Increase the air flow-rate until a maximum background current is obtained.

(4) Leave the crystal to burn in this way for about 5 min, then reduce the air flow-rate to obtain a background current of about 1×10^{-11} A.

(5) Leave running for about 1 h or until steady conditions are obtained.

(6) Reset the air flow-rate to 100 ml/min and adjust the probe height for maximum background current. If the crystal is correctly conditioned, a background current of 5×10^{-12} to 5×10^{-11} A should be obtained.

(7) Set optimum conditions for the performance required.

Using this technique it was found that a sufficiently large background signal for testing the response was obtained with a wide range of operating conditions but the loss of RbCl only occasionally became high enough to alter the shape of the crystal significantly. Where that did occur the set of measurements was completed after allowing the system to stabilise, but a new crystal was conditioned as above before proceeding further. This would not be necessary for routine use of the detector, as a used crystal (including one giving erratic signals due to a worn RbCl surface) can be reconditioned several times using the same technique. Usually it is then necessary to increase the nitrogen and/or hydrogen flow-rates in order to burn away the crystal significantly. When this procedure is used the setting of the probe height for a particular mode of operation will usually change slightly.

Most of the measurements were carried out using 1-μl injections of hexane solutions of triethyl phosphite, dibutyl sulphide, *o*-toluidine and tetradecane. These compounds were chosen to allow easy interpretation of the results, each containing only one atom of one of the elements of interest. They are also well separated on the OV-17 column at 120°–140° and simultaneous injections are possible.

Concentrations of 1 to 1×10^4 μg/ml were used as appropriate. Most of the results were recorded as peak areas in units of C/mole to provide correction for the differing retention times and molecular weights.

RESULTS AND DISCUSSION

A large part of the experimental work was based on plots of signal *versus* probe height such as the example shown in Fig. 1. The shape of the curves varies with the conditions used, a major factor being the range of probe heights over which a measurable response can be obtained. However, those shown are fairly typical with a background current which is relatively constant until it rapidly drops to zero when the probe is raised too far. The increased nitrogen response at higher probe settings was observed for a wide range of gas flow-rates but the relative sizes of the P, S and N signals vary considerably, allowing the selectivity of the detector to be altered.

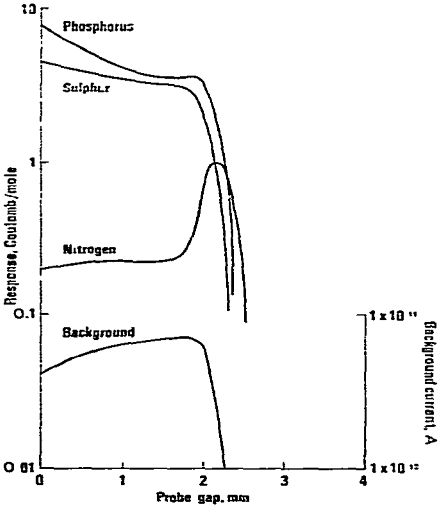
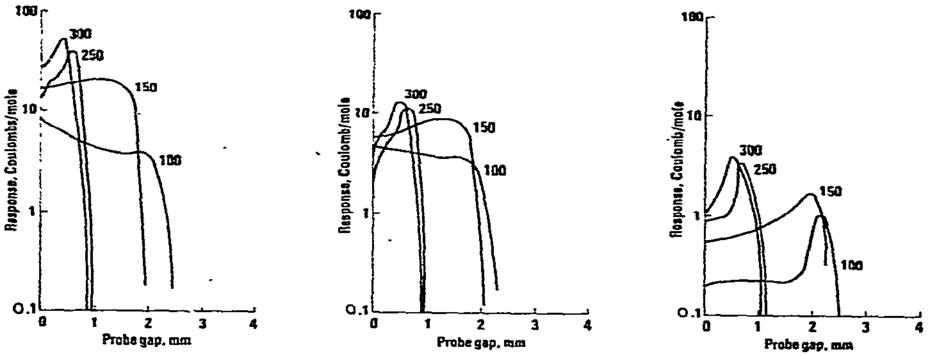


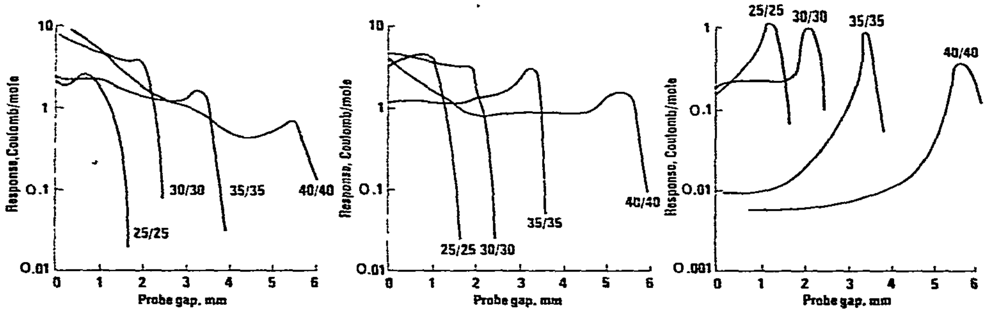
Fig. 1. Variation of detector response with probe height. Flow-rates: air, 100 ml/min; nitrogen, 30 ml/min; hydrogen, 30 ml/min.

The results obtained from these plots of signal *versus* probe height are summarized in Fig. 2 (effect of air flow-rate), Fig. 3 (effect of total hydrogen and nitrogen flow-rate) and Fig. 4 (effect of nitrogen–hydrogen flow-rate ratio). Increased air flow-rate was found to increase the maximum attainable response while reducing the range of probe heights for which a response can be obtained. This effect continues up to the maximum of 550 ml/min air obtainable from the gas control unit, but the effect of probe movement was too critical above about 300 ml/min to obtain reproducible plots. Increasing the total (hydrogen + nitrogen) flow-rate had the converse



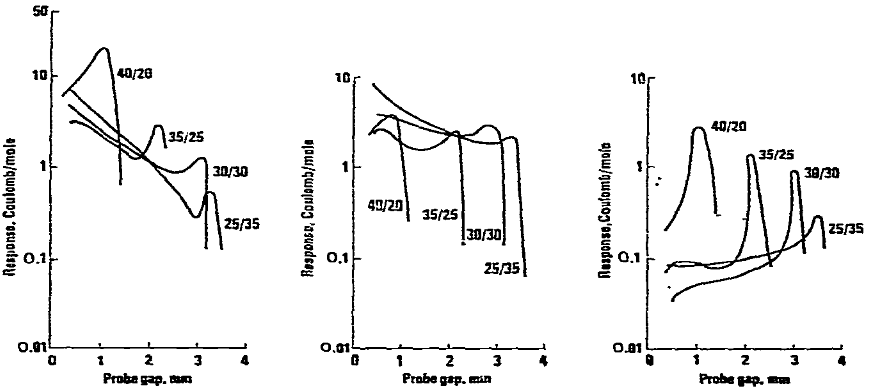
(a) PHOSPHORUS COMPOUNDS (b) SULPHUR COMPOUNDS (c) NITROGEN COMPOUNDS

Fig. 2. Detector response at different air flow-rates. Air flow-rates shown in ml/min. Hydrogen flow rate, 30 ml/min; nitrogen flow-rate, 30 ml/min.



(a) PHOSPHORUS COMPOUNDS (b) SULPHUR COMPOUNDS (c) NITROGEN COMPOUNDS

Fig. 3. Detector response at different total (hydrogen + nitrogen) flow-rates. Nitrogen/hydrogen flow-rates shown in ml/min. Air flow-rate, 100 ml/min.

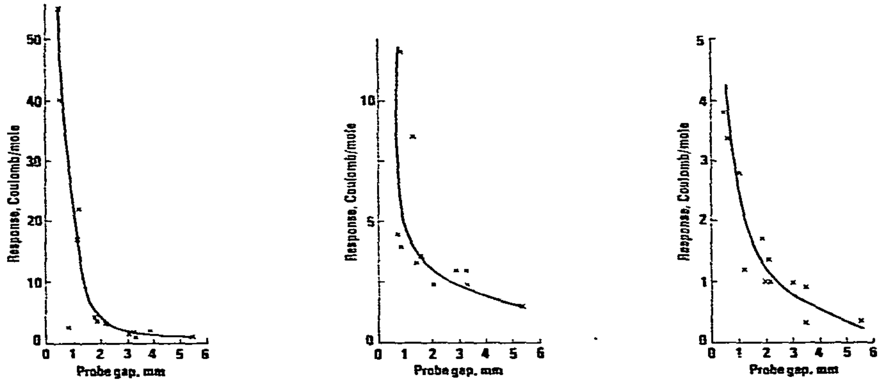


(a) PHOSPHORUS COMPOUNDS (b) SULPHUR COMPOUNDS (c) NITROGEN COMPOUNDS

Fig. 4. Detector response at different nitrogen/hydrogen ratios. Nitrogen/hydrogen flow-rates shown in ml/min. Air flow-rate, 100 ml/min.

effect on usable probe range, *i.e.*, the range increases with flow-rate, while the sensitivity decreases somewhat (particularly for phosphorus). A total of 60 ml/min seems to offer a useful probe range for many purposes (with air at 100 ml/min) and was used to test the effect of nitrogen/hydrogen ratio. As shown in Fig. 4, the range of usable probe heights increases as the mixture is varied from nitrogen rich to hydrogen rich. At the same time, phosphorus and nitrogen compounds show a considerable drop in sensitivity, whereas that for sulphur compounds remains fairly constant. Thus use of a hydrogen rich flame allows operation of the detector in its most sulphur specific mode.

While recording the data for these plots, it was realised that they showed a steady trend: the smaller the probe gap corresponding to the maximum of a particular plot, the greater the sensitivity at that maximum. This effect appears to be independent of the combination of the other variables leading to a maximum at any given probe height. The consistency of this trend can be seen in Fig. 5 in which all the points plotted correspond to maxima of the plots in Figs. 2–4. Thus if the sole objective when setting up the detector is maximum sensitivity, it should be used with the probe in its lowest position and the other variables adjusted to give optimum performance at this point.

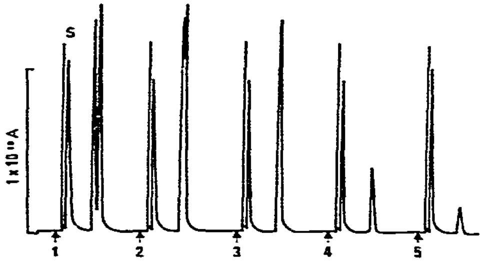


(a) PHOSPHORUS COMPOUNDS (b) SULPHUR COMPOUNDS (c) NITROGEN COMPOUNDS

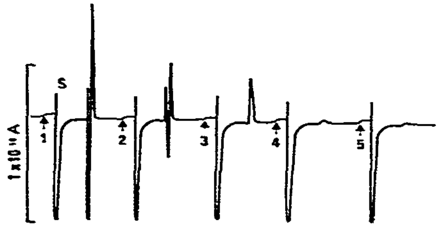
Fig. 5. Dependence of maximum attainable detector response on probe height. Each point on the curves represents one of the maxima obtained on the curves in Figs. 2–4.

The variation of detector response to hydrocarbon compounds was not included in the above measurements even though it is of considerable importance from the point of view of detector specificity. This was unavoidable because of the complex variation of the hydrocarbon peak shape with both quantity injected and small variations of the probe height of the detector. Some idea of the situation can be obtained from Fig. 6 which shows chromatograms for tetradecane injected in quantities of 0.5–50 µg with three slightly different detector settings. It can be seen that the response may vary from a normal "positive" peak, through various stages of "reversal" (in which the peak is split into two by a central trough), until it becomes completely "negative". Furthermore this change can occur either with injected quantity at one detector setting (Fig. 6b) or at one concentration as a result of small changes of probe height (*e.g.*, the 5- or 10-μg injections of Fig. 6). As a general rule, the hydrocarbon response (positive or negative) will be larger at higher probe settings but there is considerable variation, depending on the flame conditions. Fig. 6 also illustrates that, because of the effect of concentration, the solvent peak does not automatically indicate the type of hydrocarbon response to be expected from samples. However, with practice it can often give useful information on the mode in which the detector is operating (see below).

(a) Probe at 1.22mm



(b) Probe at 0.75mm



(c) Probe at 0.55mm

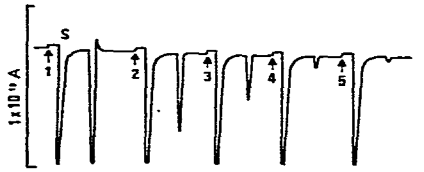


Fig. 6. Variation of hydrocarbon peak shape with concentration. Flow-rates: air, 100 ml/min; nitrogen, 30 ml/min; hydrogen, 30 ml/min. S = solvent (hexane) peak. Injected quantities of *n*-dodecane: 1 = 50 μg, 2 = 10 μg, 3 = 5 μg, 4 = 1 μg, 5 = 0.5 μg.

The effects of concentration on peak shape can also be seen to a lesser extent with compounds other than hydrocarbons once their linear response range is exceeded. This is particularly true of sulphur compounds and can result in chromatograms which can be highly misleading to the unwary. The effect is illustrated in Fig 7 which shows a set of injections of dibutyl sulphide at levels from 0.1 to 10 μg under detector conditions giving a narrow range of linear response for sulphur (see below). The retention time of the dibutyl sulphide is marked C and the solution also contains three trace sulphur-containing impurities (marked A, B and D) which were present in the sample. The first injection (0.1 μg) is approaching the limit of linear calibration for the main peak C under the conditions used and B and D are just apparent. This

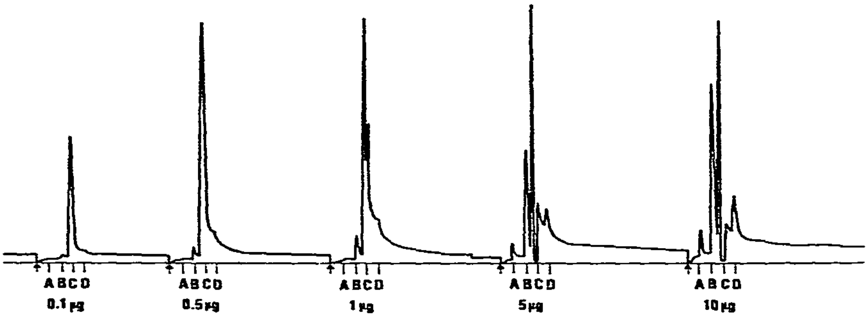


Fig. 7. Variation of sulphur peak shape with concentration. Flow-rates: air, 100 ml/min; nitrogen, 25 ml/min; hydrogen, 35 ml/min.

is the type of chromatogram the user would expect to obtain from this sample. At 0.5 µg, C has increased in height but the response is obviously non linear. B and D have increased as expected and A is now just apparent. By 1 µg A, B and D are still showing a normal, linear response but C is well into the "reversed" region and no longer increases in height. It could easily be mistaken for two partially resolved peaks. At 5 µg the "reversal" of C is complete; the centre now reaches zero and the right hand side has almost been lost. It has the appearance of another impurity giving a severely tailing peak. The left hand side is easily mistaken for a normal, well-resolved

TABLE II

COMPARISON OF FID AND THERMIONIC DETECTOR SENSITIVITIES

Responses are given in C/mole (signal measured as peak area) and in A/ng (signal measured as peak height and without any correction for the differing retention times of the test compounds); the latter are presented in parentheses.

Parameter	*Thermionic detector set to maximum sensitivity* for:*		*FID*
	Phosphorus and nitrogen	*Sulphur*	
Air flow-rate (ml/min)	550	450	400
Nitrogen flow-rate (ml/min)	68.0	68.0	25
Hydrogen flow-rate (ml/min)	34.0	34.5	25
Probe gap	zero	zero	
Background current (A)	1.2×10^{-9}	9.0×10^{-10}	8.0×10^{-12}
Background noise level (A)	1.0×10^{-12}	2.0×10^{-13}	2.0×10^{-14}
Triethyl phosphite response	3150	400	0.8
	(3.1×10^{-9})	(4.0×10^{-10})	(1.0×10^{-12})
Dibutyl sulphide response	3.0	15.0	1.50
	(2.5×10^{-12})	(1.2×10^{-11})	(1.3×10^{-12})
o-Toluidine response	13.5	2.2	1.0
	(9.2×10^{-12})	(1.5×10^{-12})	(7.5×10^{-13})
Tetradecane response	0.5	−0.2	2.4
	(7.5×10^{-14})	(-3×10^{-14})	(7.0×10^{-13})

* This does not necessarily correspond to a setting recommended for optimum detector performance (see text).

TABLE III

USEFUL OPERATING MODES OF THE THERMIONIC DETECTOR

Mode	*Probe position**	*Flame condition (flow-rate in ml/min)***			*Advantages*	*Disadvantages*	*Comment*
		Air	*Nitrogen*	*Hydrogen*			
1	Zero	550	68–70	34–35	Maximum sensitivity to P- and N-compounds with extremely sensitive, selective response to P-compounds in particular	Rapid consumption of crystal. Relatively poor stability and high noise level.	Should only be used for routine work when maximum sensitivity is essential.
2	Zero	450	68–70	34–35	Maximum sensitivity to S-compounds	As 1	As 1
3	Low	300	30	30	High sensitivity with high discrimination against hydrocarbons (which give a negative response)	Crystal consumption still high. Probe setting critical because of restricted usable range and rapid variation with probe height of the relative response to P, N or S.	Better than 1 and 2 but may cause problems when used routinely. Note that maximum sensitivity is not obtained simultaneously at one probe setting for all three types of compound.
4	Medium	250	30	30	Allows simultaneous determination of P-, N- and S-compounds with similar sensitivity while discriminating against hydrocarbons.	Sensitivity is similar to FID, but well below that attainable for each type of compound individually. Hydrocarbon response is positive, so that better selectivity against hydrocarbons can be obtained for each type of compound individually.	Satisfactory for routine use provided care is taken to standardise setting-up and operating techniques. Very useful for many trace analysis problems such as pesticide or drug residues.

5	High	100	30	30	As 4	As 4, except sensitivity is somewhat poorer.	As 4, except that operation in this mode is more convenient and stable. Particularly useful for long term operation with minimum attention.
6	High	100	25	35	Gives a selective response to S compounds against P and N compounds as well as hydrocarbons	Linearity range for S is restricted. Sensitivity well below maximum attainable for S.	Easy to use routinely. The linearity range for S can be increased by increasing the background (*e.g.*, increase hydrogen flow-rate) at the expense of less selectivity against P. This also considerably improves selectivity against N.
7	Medium to high	300	30	30	Gives a selective response to N compounds against P and S compounds as well as hydrocarbons	Better selectivity against hydrocarbons obtainable under other conditions. Much better sensitivity can be obtained if a larger P response can be tolerated.	Better for regular use than 3 because of the lower background current but the restricted range of probe movement means that practice is needed to set up this mode reproducibly.

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* Relative to the range available under the flame conditions in use.

** These are intended only as a guide; the hydrogen flow-rate in particular should be optimised (see text).

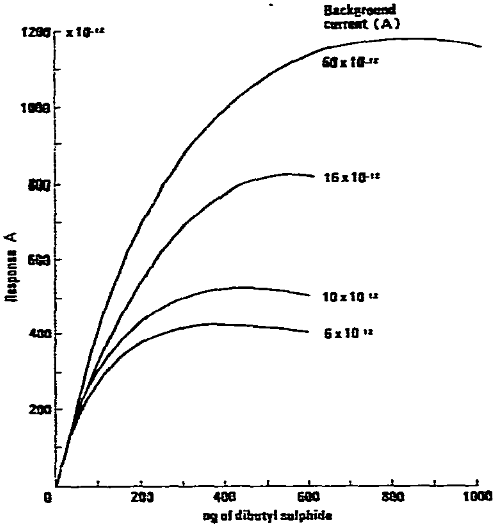

Fig. 8. Calibration curves for dibutyl sulphide at various background currents. Flow-rates: air, 100 ml/min; hydrogen, 28.5 ml/min. The nitrogen flow-rate was varied between 35 and 55 ml/min to obtain the range of background currents shown. The response was measured as the peak height.

peak. The three impurities continue to show a linear response. Finally at 10 µg there is little further change in C but B is now beyond the linear part of the calibration; at higher concentrations it, too, would begin to reverse.

Although similar effects are sometimes seen for P- and N-containing compounds, these give a much wider linear calibration range and problems would not usually arise under the conditions used to determine them. Even with sulphur compounds it is possible to extend the range of linearity (and increase the sensitivity) by working with a larger background current. This is apparent from Fig. 8 which shows a set of calibration curves for dibutyl sulphide obtained with detector background currents between 6×10^{-12} A (approximately the value in the chromatograms in Fig. 7) and 6×10^{-11} A.

In addition to its ability to give a selective response, the thermionic detector is widely recommended for its ability to show an enhanced sensitivity to certain compounds compared with the normal FID. The results shown in Table II represent the maximum sensitivity we were able to obtain with the detector but they could probably be improved by altering the shape of the crystal (by varying the conditioning procedure) to increase the background current. It can be seen that by far the greatest enhancement (several thousand fold) occurs with the phosphorus compounds for which the detector was originally recommended. For sulphur and nitrogen compounds the enhancement is much smaller (around ten fold) and from the point of view of detection limits is off-set by the higher signal noise levels. Thus for these compounds the detector is mainly of value for its selectivity. Although the sulphur response has been known for some time[11,12], it is only recently that it has been recognised[13,14] as of similar analytical utility to the widely used nitrogen response. Thus the data reported here for sulphur is of considerable practical importance. It should be emphasized, however, that the conditions used to obtain the maximum sensitivities for all of the compounds in Table II are not normally suitable for routine operation of the detector for long periods. The high background current obtained (about 1×10^{-9} A) results from rapid vaporization of the RbCl crystal. Thus detector performance shows a steady drift, the crystal needs frequent replacement and it is necessary to remove RbCl from the collector electrode and the jet at regular intervals.

A more useful approach to routine use of the detector is to identify some of the possible modes in which it may be operated and then to select the most appropriate for any particular application, remembering that it is not usually possible to obtain maximum sensitivity, maximum selectivity and maximum convenience of use simultaneously even for just one compound. Table III represents an attempt to list some of the possibilities based on the results given above and our own experience with the detector. They were mostly designed to deal with particular problems and many other useful sets of operating conditions could probably be devised. The recommendations

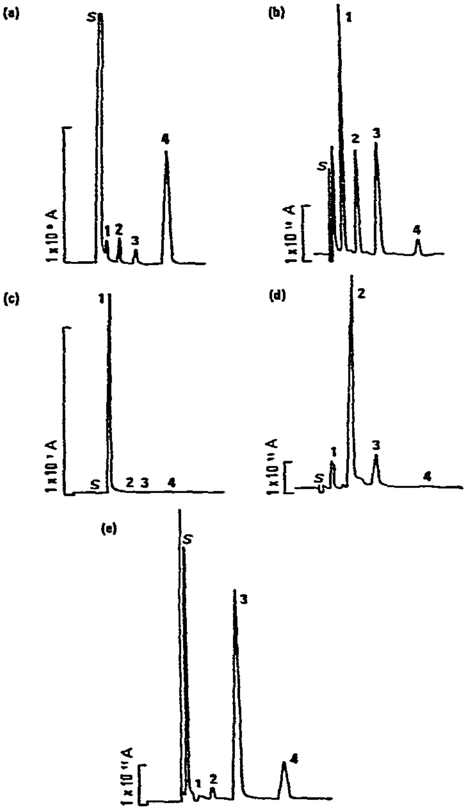

Fig. 9. Comparison of the response of an FID and the thermionic detector operated in different modes of selectivity. Flow-rates (ml/min) of air, nitrogen and hydrogen in Figs. a–e are given in this order: (a) FID; 465, 25.0, 26.4. (b) TD in general mode; 250, 30.0, 29.2; probe gap, 1.37 mm. (c) TD in phosphorus-selective mode; 550, 68.0, 34.0; probe gap, zero. (d) TD in sulphur-selective mode; 100, 25.0, 34.6; probe gap, 3.60 mm. (e) TD in nitrogen-selective mode; 300, 30.0, 29.8; probe gap, 1.22 mm. Peak identification: S = solvent, 1 = triethyl phosphite (100 ng), 2 = dibutyl sulphide (100 ng), 3 = *o*-toluidine (100 ng), 4 = tetradecane (1000 ng).

in Table III can only be used as a guide since even with one detector the results obtained will vary with factors such as the way the crystal is inserted in its holder, its previous operating history and the accuracy with which the probe height is reset. A useful approach is to decide on the performance required, set the air, nitrogen and hydrogen flow-rates to the recommended values and position the probe in approximately the right area (*i.e.*, low, medium, high, etc.) using the variation of background current as a guide. Then using a suitable test mixture (*e.g.*, of P-, S- and N-containing compounds as in this paper) adjust the probe height until the detector is operating in the required mode. Finally, optimise the performance by very small adjustments to the hydrogen flow-rate. In most cases it is far easier to optimise the detector and understand its operation if these tests are made with a suitable mixture rather than by injecting just standard solutions of the sample compound. When the detector is in regular use for long periods, it will be found most convenient if satisfactory performance can be achieved using low background currents (*i.e.*, low air flow-rates or a high probe) to minimise loss of RbCl. In addition, use of low air flow-rates extends the range of probe heights over which the detector operates and greatly facilitates accurate positioning and resetting of the probe.

The variety of operating conditions which can be achieved is illustrated by Fig. 9 which compares the chromatogram obtained using an FID for a standard mixture with some of the thermionic detector modes listed in Table III. For routine application of the detector to pesticide residue analysis we have found the general mode to be particularly useful. It offers similar sensitivity to the FID for P-, S- or N-containing pesticides with considerable discrimination against the solvent and sample co-extractives. In fact several different versions of this mode can be used depending on the requirements for sensitivity and long term stability and the concentrations of the coextractives in the injected sample.

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REFERENCES

1 A. Karmen and L. Giuffrida, *Nature (London)*, 201 (1964) 679.
2 V. V. Brazhnikov, M. V. Gur'ev and K. I. Sakodynsky, *Chromatogr. Rev.*, 12 (1970) 1.
3 W. A. Aue, *Advan. Chem. Ser.*, 104 (1971) 39.
4 D. J. David, *Gas Chromatographic Detectors*, Wiley-Interscience, New York, 1974, Ch. 5.
5 J. Ševčík, *Detectors in Gas Chromatography*, Elsevier, Amsterdam, 1976, Ch. 6.
6 B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1974) 625.
7 W. P. Cochrane and R. Greenhalgh, *Chromatographia*, 9 (1976) 255.
8 G. R. Verga and F. Poy, *J. Chromatogr.*, 116 (1976) 17.
9 F. P. Speakman, *Column*, 3 (1968) 2.
10 D. F. K. Swan, *Column*, 14 (1972) 9.
11 M. Dressler and J. Janák, *Collect. Czech. Chem. Commun.*, 33 (1968) 3970.
12 M. Dressler and J. Janák, *J. Chromatogr. Sci.*, 7 (1969) 451.
13 N. Mellor, *J. Chromatogr.*, 123 (1976) 396.
14 R. A. Hoodless, M. Sargent and R. D. Treble, *Analyst (London)*, 101 (1976) 757.