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A STUDY OF THE STABILITY OF A NITROGEN-SELECTIVE THERMIONIC DETECTOR

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SUMMARY

The stability of a thermionic detector fitted with a rubidium chloride tip has been studied by comparison with the performance of a conventional flame ionisation detector. The variations of response of the detectors to a given set of conditions over an extended period of time have been measured. Values for sensitivities and detection limits are quoted, based on the response to trace amounts of dialkylnitrosamines.

INTRODUCTION

The thermionic detector was first described by Karmen and Giuffrida[1] in 1964, who showed that by seeding the flame of a flame ionisation detector with a sodium salt some selectivity towards organophosphorus compounds was obtained. Further developments revealed that the most satisfactory response to phosphorus was obtained when caesium bromide was introduced into the flame. By the use of other salts of Group I metals some selectivity toward other elements is obtained[2]; rubidium chloride is suitable for use in the nitrogen-selective mode[3].

The thermionic detector has been used extensively for the detection of organophosphorus pesticides[4–9]. Several papers concerned with the use of the detector with nitrogen and sulphur compounds have also been published[8–13], but no work on the reproducibility of the detector response to a given N or S containing mixture over a period of time has been reported. This factor is clearly important to routine analysis. It is the purpose of this work to compare the performance and stability of a rubidium chloride thermionic detector and a conventional flame ionisation detector under fixed gas chromatographic conditions.

It is prerequisite for any routine analysis that the setting of the equipment prior to analysis must occupy a negligible amount of time, and that once set, reliable results must be obtained over a reasonable period of time. It has been noted by several authors that the response of salt tip detectors is severely affected by minor changes in gas flow-rate, the condition of the salt tip, the height of the tip above the burner, and other aspects of detector geometry[3,14]. The stability of the detector has been followed after initial setting of the above parameters for optimum response.

EXPERIMENTAL

A Pye 104 Chromatograph fitted with thermionic (TD) and flame ionisation detectors (FID) was used. The thermionic detector has a three-electrode configuration[13] and consists of a probe mounted centrally within a perforated cylinder. Housed in the open end of the cylinder is a rubidium chloride annulus. This assembly is placed vertically into the detector body so that the salt tip lies above the burner head. The position of the rubidium chloride tip above the flame may be varied. The detectors were connected in parallel via a 1:1 splitter at the column exit. The carrier gas flow-rate through the column was chosen to give good resolution between a series of dialkylnitrosamines. A second gas stream was introduced between the column exit and splitter, and was adjusted to give optimum detector response. The hydrogen flow-rate to the detector was found to be particularly critical and it was necessary to stabilise the flow using a pressure regulator (Watts Type M). The optimum position of the salt tip above the burner was established for dimethylnitrosamine. The position of the tip for maximum response varied with time, and was reset daily. All other parameters were fixed throughout the period of study. The operating conditions are given in Table I.

TABLE I

OPERATING CONDITIONS

Column: 5.1 m × 2 mm I.D. stainless steel, packed with 15% FFAP on 80–100 BS mesh acid-washed Chromosorb W.

	Temperature (°C)			*Flow-rate (ml/min)*	
	TD	*FID*		*TD*	*FID*
Injection port	160	160	Air	250	275
Column	160	160	Hydrogen	27	43
Detector	250	250	Nitrogen at detectors	32	32
			Nitrogen at column exit	— 14	—

A primary standard solution containing 100 μl/l of dimethyl-, diethyl-, and dipropylnitrosamines (DMN, DEN and DPN) in water was used throughout the study. 3-μl aliquots of this and other standards, prepared by dilution, were injected daily over a period of several weeks in order to follow the variations of response of the two detectors.

RESULTS AND DISCUSSION

Since the system was operated under fixed conditions with a constant sample size, the stabilities and absolute responses of the two detectors may be directly compared. Comparisons were made on the basis of peak area measurements. Graphs of detector response for each nitrosamine against its concentration were plotted for each daily set of runs. Examples are shown in Figs. 1–3. Over the range studied (5–50 μl/l per detector) response was sensibly linear. Variations of response, expressed in terms of sensitivity[15], are presented in Table II. The results are derived from 126 determinations per compound, made over a period of 5 weeks.

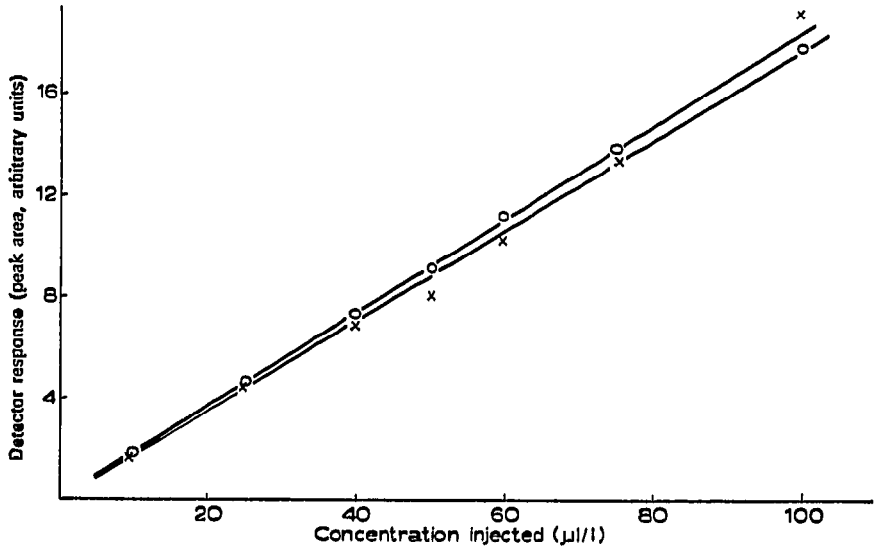

Fig. 1. Response to DMN. ⊙, FID; ×, TD.

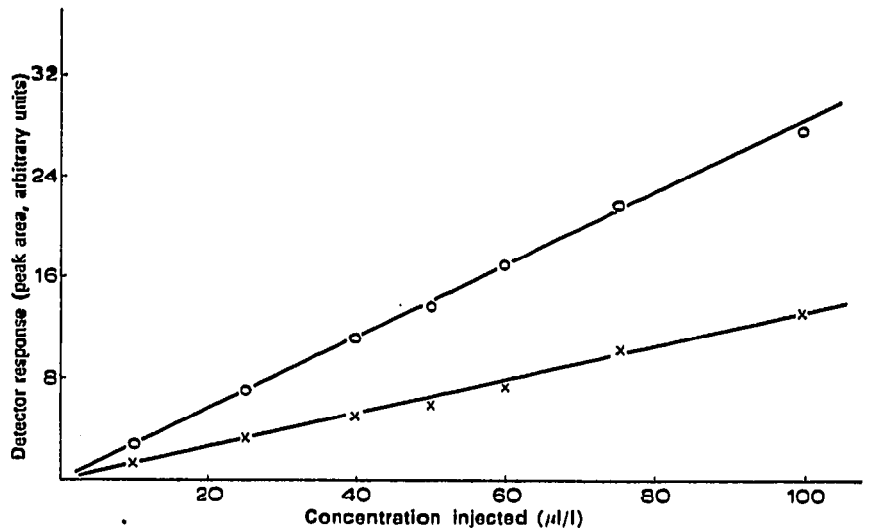

Fig. 2. Response to DEN. ⊙, FID; ×, TD.

It is clear from Table II that the FID is far more stable than the TD and that for nitrosamines at least the absolute response of the FID is somewhat higher than that of the nitrogen-selective detector. Measurement of the response of the TD to dimethylnitrosamine and hexane showed that the response to the nitrosamine was 10^4 greater than that to an equal volume of hexane. Response of the TD to fenitrothion, a nitrogen- and phosphorus-containing pesticide, was two orders of magnitude higher at 1.50×10^{-1} A sec g^{-1}; azobenzene gave a value of 3.3×10^{-2} A sec g^{-1}.

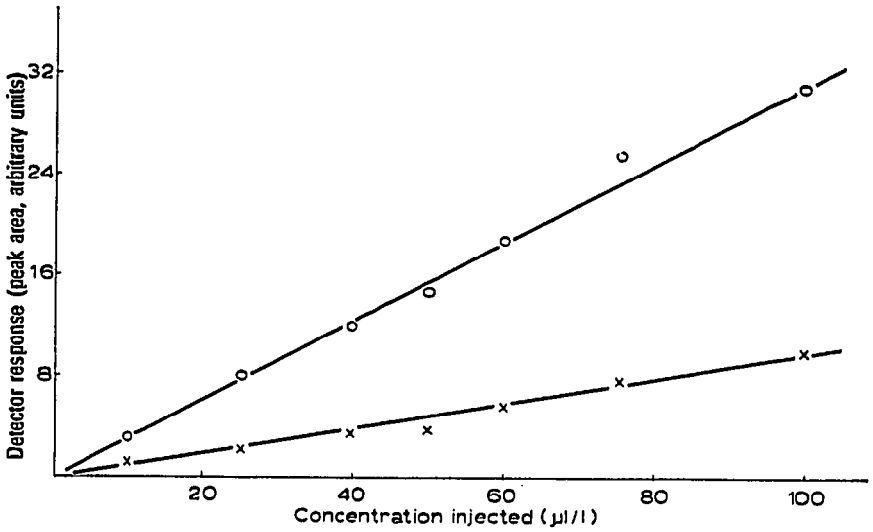

Fig. 3. Response to DPN. ⊙, FID; ×, TD.

TABLE II

VARIATIONS OF SENSITIVITIES OF TD AND FID

Compound	*TD*		*FID*	
	Mean sensitivity ($A\ sec\ g^{-1}$)	*Coefficient of variation* (%)	*Mean sensitivity* ($A\ sec\ g^{-1}$)	*Coefficient of variation* (%)
DMN	2.60×10^{-3}	19.1	3.82×10^{-3}	3.2
DEN	1.98×10^{-3}	20.3	6.32×10^{-3}	3.5
DPN	1.53×10^{-3}	20.1	7.28×10^{-3}	3.9

An examination of the response of the TD with ageing of the tip showed that as the gap for optimum response increased the absolute response decreased. This is illustrated in Fig. 4, which covers an 8-day period. Even after prolonged periods of operation, detector response could be returned to its original value by cleaning the probe, with the tip in position. A comparison of the sensitivity of a cleaned detector, with a 4-week interval between determinations, is given in Table III.

TABLE III

SENSITIVITY OF TD WITH A CLEANED PROBE

Compound	*TD*		*FID*	
	Initial sensitivity ($A\ sec\ g^{-1}$)	*Sensitivity after 4 weeks* ($A\ sec\ g^{-1}$)	*Initial sensitivity* ($A\ sec\ g^{-1}$)	*Sensitivity after 4 weeks* ($A\ sec\ g^{-1}$)
DMN	3.77×10^{-3}	3.71×10^{-3}	3.86×10^{-3}	3.88×10^{-3}
DEN	2.95×10^{-3}	2.84×10^{-3}	6.15×10^{-3}	6.17×10^{-3}
DPN	2.17×10^{-3}	2.36×10^{-3}	7.30×10^{-3}	6.66×10^{-3}

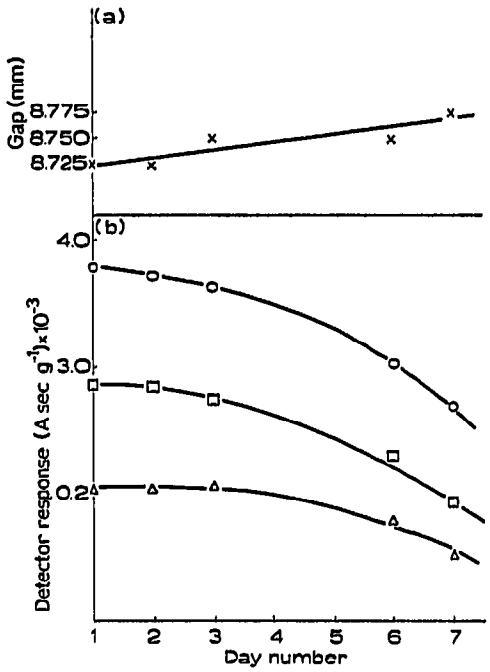

Fig. 4. (a) TD probe gap. (b) TD response. ⊙, DMN; ⊡, DEN; △, DPN.

There is some disagreement in the literature as to whether TD response is a function of the proportion of phosphorus, sulphur or nitrogen in the compound[16–18]. Recent work has shown that, additionally, response is a function of the structure of the compound[9]. Observed and predicted response factors for DEN and DPN, based on the observed response of DMN, are given in Table IV, from which it can be seen that, within this series, response is a function of nitrogen content.

TABLE IV

TD RESPONSE FACTORS

Compound	*Measured response*	*% Nitrogen in compound*	*Calculated response*
DMN	1.00	37.8	1.00
DEN	0.76	27.5	0.73
DPN	0.59	21.5	0.57

The repeated injection of standard solutions is not representative of a typical analysis, for example for the determination of trace constituents in extracts of food. Figures for reproducibility quoted in Table II are therefore the most favourable that can be expected. Injections of extracts from which relatively large amounts of extraneous matter are also eluted may interfere with the subsequent response and stability of the TD. Approximately 400 μl of extracts were injected over a period of

several days, after which the probe was cleaned and response to the standard solutions measured. This procedure was repeated at weekly intervals covering a period of 5 weeks. Results are given in Table V.

TABLE V

EFFECT OF EXTRANEOUS MATERIAL ON DETECTOR RESPONSE

Compound	*TD*		*FID*	
	Mean sensitivity (A sec g^{-1})	*Coefficient of variation (%)*	*Mean sensitivity (A sec g^{-1})*	*Coefficient of variation (%)*
DMN	3.90×10^{-3}	30.7	3.73×10^{-3}	4.0
DEN	2.84×10^{-3}	30.9	6.17×10^{-3}	2.8
DPN	2.12×10^{-3}	34.6	6.52×10^{-3}	5.0

Comparison with Table III reveals that the sensitivities of the two detectors have not been affected.

Detection limits (Q_0 values) have been calculated using the equation $Q_0=2R/S$, where S=sensitivity in A sec g^{-1} and R=noise level in A.

Noise was measured regularly for both detectors over a period of 6 weeks, and was 3.3×10^{-14} A for the FID and 5.6×10^{-13} A for the TD. There was no change with the ageing of salt tip and no change after the injection of the extracts of foods. The detection limits quoted in Table VI refer to a cleaned probe.

TABLE VI

DETECTION LIMITS

Compound	*TD*		*FID*
	g sec^{-1}	*g Nitrogen sec^{-1}*	*g sec^{-1}*
DMN	2.97×10^{-10}	1.12×10^{-10}	1.70×10^{-11}
DEN	3.80×10^{-10}	1.04×10^{-10}	1.07×10^{-11}
DPN	5.18×10^{-10}	1.12×10^{-10}	0.99×10^{-11}

CONCLUSIONS

Variations of response of the TD are significantly higher than those of a conventional flame detector. The sensitivity of the TD falls with age, but can be restored by cleaning the probe. For some simple nitrosamines response is a function of nitrogen content. Analysis of dirty extracts does not subsequently affect the sensitivity of the TD.

The noise level and detection limits for the nitrosamines are at least an order of magnitude higher on the TD than on the FID.

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