

THE CRITICAL EXAMINATION OF COMMERCIALY AVAILABLE DETECTORS FOR USE IN GAS CHROMATOGRAPHY

PART I. THE MACRO ARGON AND FLAME IONISATION DETECTORS

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INTRODUCTION

Due to the increasing interest in the quantitative accuracy that can be obtained in gas chromatographic analyses, a precise knowledge of the characteristics of commercially available detectors is essential. This paper, which is the second of a series concerned with the investigation of these characteristics, gives the results from the detailed study of two detectors, the Macro Argon Detector, Pye Cat. No. 12216, and the Flame Ionisation Detector, Pye Cat. No. 12210 (manufactured to a design by Ionics Inc.). The response of each detector was examined over a wide range of concentration levels using a method of assessment previously described in this journal¹. Where possible, operating conditions are given for each detector, over which satisfactory quantitative results can be obtained. The experimental work was confined to conditions normally employed in the practice of gas chromatography.

EXPERIMENTAL

The apparatus used, together with the theory of the dilution system employed, has been described by FOWLIS AND SCOTT¹. The response of each detector was examined using diisopropyl ether, *n*-heptane, toluene and chlorobenzene at various flow-rates and operating temperatures. However, each detector has its own specific operating parameters other than those of the chromatographic equipment with which it is associated, so prior to each test the voltage, temperatures and flow-rates were adjusted to the value required and known masses of the solutes placed in the dilution vessel. The peak height, equivalent to a current or voltage signal produced by the detector, was measured for each successive operation of the automatic sampling valve. This procedure was carried out altering each pertinent variable as required. So that the results could be presented in the form of a graph relating signal to mass of solute entering the detector, it was necessary to calculate the concentration of solute in grams per second leaving the dilution vessel and to express this in terms of mass of solute entering the detector.

A worked example for a particular set of operating conditions is given to illustrate the method employed. The concentration of solute in the exit gas is dependent on the properties of the dilution system, *viz.* partition coefficient of solute, gas and

liquid volumes of the vessel, gas flow-rate, temperature and pressure. The gas pressure in the dilution vessel was measured with a static mercury manometer, the temperature with a thermocouple immersed in the liquid and the partition coefficients of the substances concerned obtained from their retention ratios to *n*-heptane. The partition coefficients of *n*-heptane, which were taken from the results of DESTY AND GOLDUP² and EVERED AND POLLARD³, were plotted as their logarithms against the reciprocal of the absolute temperature. The partition coefficient of *n*-heptane at any temperature was taken from the regression line through these points. The temperature in the dilution vessel tended to fluctuate due to the thermal inertia in the system. The fluctuation had an amplitude of approximately $\pm 0.4^\circ$ and so the temperature was measured over a period of time and the mean value taken as the temperature of the dilution vessel. The flow-rate was measured by means of a calibrated soap-film meter, exterior to the apparatus and therefore at room temperature. This flow-rate was corrected to the temperature and pressure existing in the dilution vessel. An example of the calculation carried out for a test of the flame-ionisation detector using diisopropyl ether is given below.

Conditions

Carrier gas flow-rate: 60.0 ml/min

Hydrogen flow-rate: 60.0 ml/min

Oxygen flow-rate: 60.0 ml/min

Detector voltage: 100 V

Solute: Diisopropyl ether

Volume of liquid in the dilution (V_L): 4.93 ml.

Volume of gas in the dilution vessel (V_g): 23.07 ml

Determination of flow-rate through the dilution vessel

The mean flow-rate through the dilution vessel (5 observations) = 15.38 ml/min at 21° and 760 mm pressure.

The pressure in the dilution vessel = 769 mm Hg.

The maximum temperature of the dilution vessel = 70.10° .

The minimum temperature of the dilution vessel = 68.30° .

The mean temperature of the dilution vessel (20 observations) = 69.40° .

Thermocouple correction obtained by comparison with N.P.L. mercury in glass thermometer = $+0.5^\circ$.

The corrected temperature of the liquid in the dilution vessel = 69.9° .

Thus, the gas flow-rate through the dilution vessel at 69.9° and 769 mm pressure = 17.72 ml/min.

The partition coefficient (K_1) of *n*-heptane at 69.9° = 200.

Time for elution of air = 41.4 sec.

Time for elution of diisopropyl ether = 161 sec.

Time for elution of *n*-heptane = 445 sec.

Thus, the retention ratio of diisopropyl ether with respect to *n*-heptane = 0.296.

Hence, the partition coefficient of diisopropyl ether (K_2) at 69.9° = 59.3.

Thus

$$V_g + K_2 V_L = 315.3 \text{ ml}$$

Hence

$$\frac{Q}{V_g + K_2 V_L} = 5.62 \cdot 10^{-2} \text{ min}^{-1}$$

The weight of diisopropyl ether placed in the dilution vessel was $5.4 \cdot 10^{-3}$ g. Thus, the initial concentration of diisopropyl ether in dilution vessel exit gas is

$$\frac{\text{mass}}{V_g + K_2 V_L} = 1.71 \cdot 10^{-5} \text{ g/ml}$$

Gas volume equivalent to peak width at base = 20.8 ml.

Assuming the concentration of solute in the carrier gas at the peak maximum is twice the average concentration in the peak and 1-ml samples of exit gas from the dilution vessel are placed on the column, then the concentration of solute in the detector at the peak maximum, X_{gn}^o ,

$$X_{gn}^o = \frac{1.71 \times 10^{-5} \times 2}{20.8} = 1.65 \cdot 10^{-6} \text{ g/ml}$$

(assuming the first sample is taken at $t = 0$).

Thus,

$$\text{since } X_{gt} = X_{g0} \exp \left[- \left(\frac{Qt}{V_g + K_2 V_L} \right) \right],$$

a graph of $\log X_{gt}$ against time (t) can be constructed. From this graph values of solute concentration in g/ml at the peak maximum for each sample were calculated and results presented as a graph of \log_{10} solute concentration against \log_{10} detector current. If the slope of this graph is unity, then the detector has a linear response.

Since the column flow-rate was 60.0 ml/min, the mass of solute entering the detector in unit time is numerically equal to the concentration in g/ml. The ionisation efficiency was calculated from the current produced when a mass of 10^{-9} g of solute entered the detector in one second.

Flame ionisation detector

A diagram of the detector is shown in Fig. 1. It is constructed of stainless steel and contains a cylindrical electrode insulated from the body by means of a Teflon sleeve. After continuous operation for about 8–10 weeks there were distinct signs of corrosion on the walls of the detector itself and on the tubular electrode. The corrosion on the electrode caused some instability and had to be removed. A more corrosion-resistant stainless steel or a good quality gold film on the inside of the detector body and over the electrode should eliminate this effect. The quality of the plating should be such that the temperature changes which occur in the detector do not cause flaking.

If concentrations near the limit of the detector sensitivity are used, good electrical shielding is required or the baseline will be unstable. The values of the noise level given were for the detector together with its ancillary equipment. The amplifier characteristics contributed a large proportion of the total noise.

Results. The presentation of the results in the form of \log_{10} ionisation current plotted against \log_{10} of the concentration simplifies the assessment of the linearity of the detector. The detector has a linear response if the slope of this curve is unity.

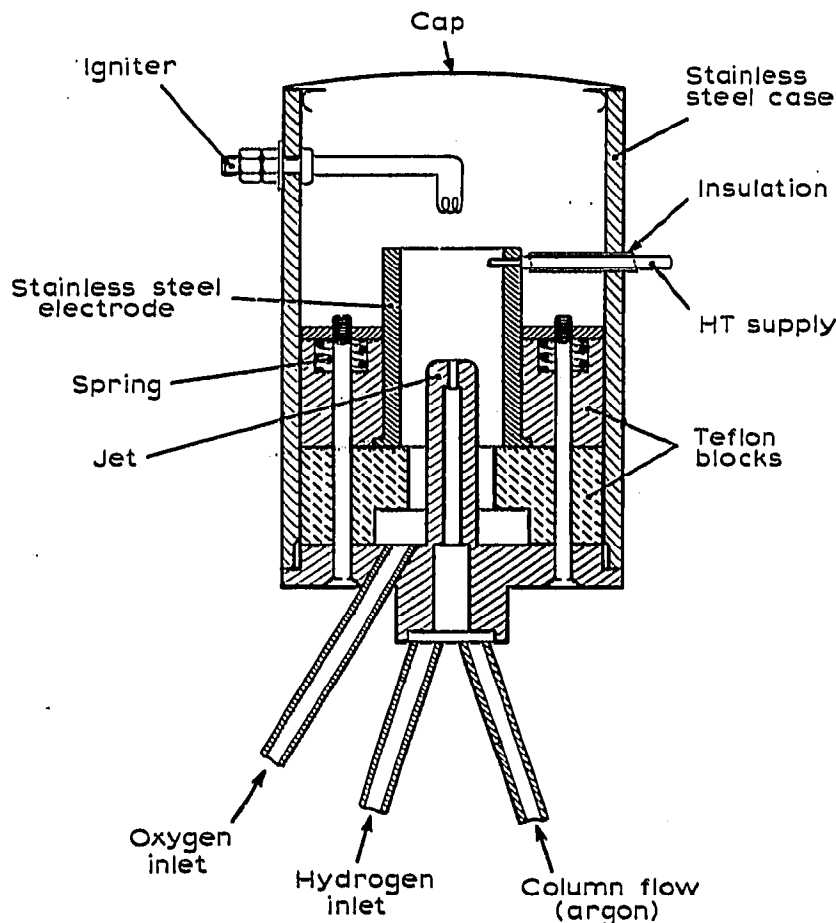


Fig. 1. Cross section of the flame ionisation detector.

If the detector response is non-linear then the slope may neither be unity nor the curve linear. The results obtained with different substances are shown in Fig. 2 (a, b, c, d) and for different operating conditions in Fig. 3 (a, b, c, d). The tables attached to Fig. 2 and 3 give detector characteristics and the experimental conditions under which these were obtained. The absolute sensitivity is taken as that concentration which will give a current equivalent to twice the noise level.

Discussion of results. The flame-ionisation detector has a linear response for the four compounds examined over a wide concentration range (10^{-6} to 10^{-10} g/ml, and is relatively insensitive to the applied voltage. The voltage range examined was 25 to 150 V, and it can be seen from Fig. 3 (d) that all the points for the various voltages lie on the same straight line, over a concentration range of four orders. Fig. 3(a) and 3(b) show that the detector is relatively insensitive to changes in column flow-rate, but if the oxygen flow is reduced below the 1:1 ratio of hydrogen to oxygen there is a tendency for the detector response to become non-linear (as shown by Fig. 3(c), where the response index is 1.13). The optimum operating conditions were found to be:

- column flow-rates up to 60 ml/min
- hydrogen flow-rate 60 ml/min
- oxygen flow-rate 60 ml/min
- applied voltage 25–150 V.

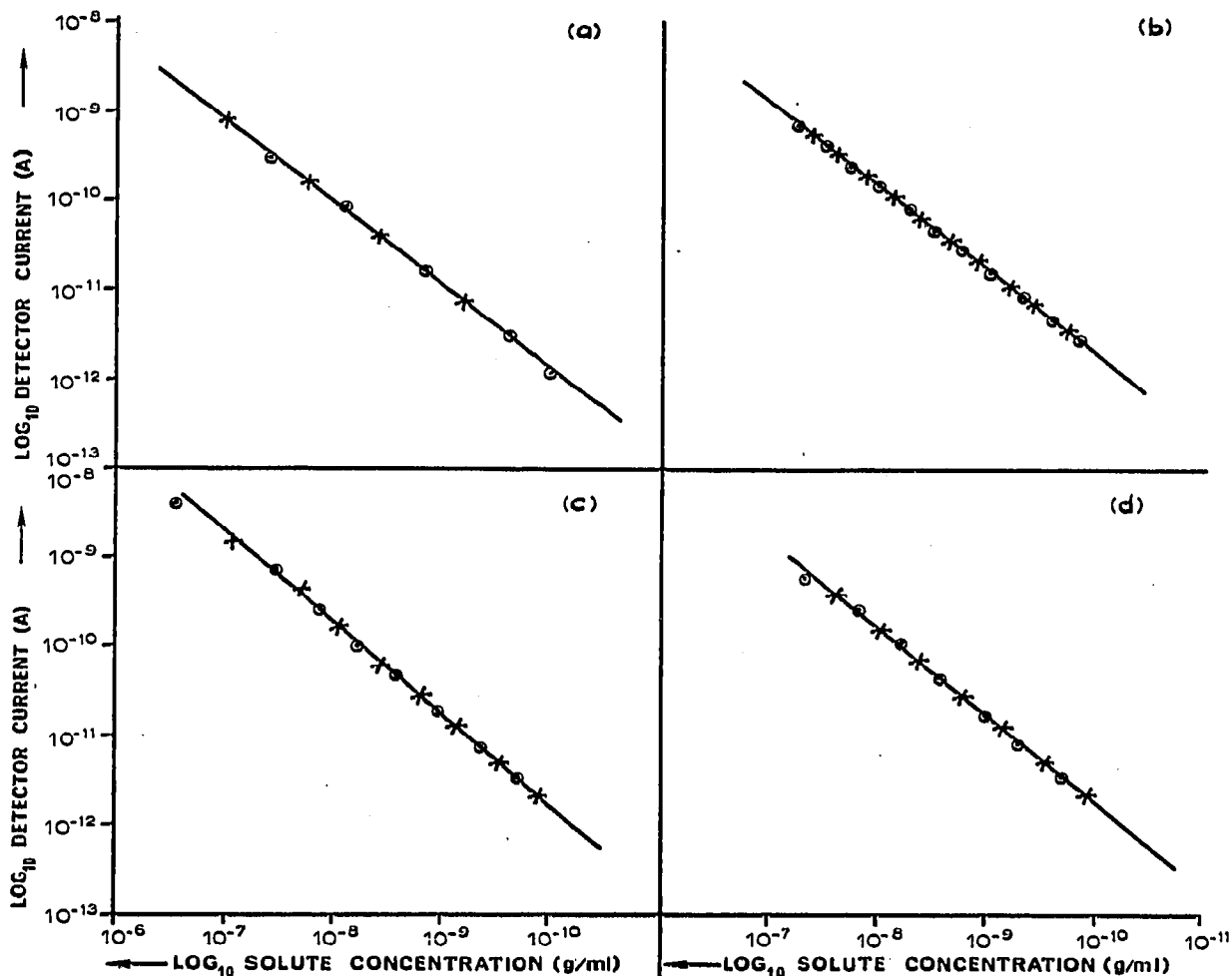


Fig. 2. Response curves for the flame ionisation detector for different solutes. Detector temperature: 23°. Solute: (a) diisopropyl ether; (b) *n*-heptane; (c) toluene; (d) chlorobenzene. Detector flow-rate: 60 ml/min. Hydrogen flow-rate: 60 ml/min. Oxygen flow-rate: 60 ml/min.

Voltage	Minimum detectable signal (estimate) g/ml	Ionization efficiency %	Response index	Range g/ml	Noise level A
(a) 50	$6.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	0.96	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
100	$6.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	0.96	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
(b) 50	$3.0 \cdot 10^{-11}$	$1.5 \cdot 10^{-3}$	1.05	$10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
100	$3.0 \cdot 10^{-11}$	$1.5 \cdot 10^{-3}$	1.05	$10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
(c) 50	$5.0 \cdot 10^{-11}$	$2.0 \cdot 10^{-3}$	0.97	$5 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
100	$5.0 \cdot 10^{-11}$	$2.0 \cdot 10^{-3}$	0.97	$5 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
(d) 50	$3.8 \cdot 10^{-11}$	$1.8 \cdot 10^{-3}$	0.98	$5 \cdot 10^{-8} - 10^{-10}$	$8 \cdot 10^{-13}$
100	$3.8 \cdot 10^{-11}$	$1.8 \cdot 10^{-3}$	0.98	$5 \cdot 10^{-8} - 10^{-10}$	$8 \cdot 10^{-13}$

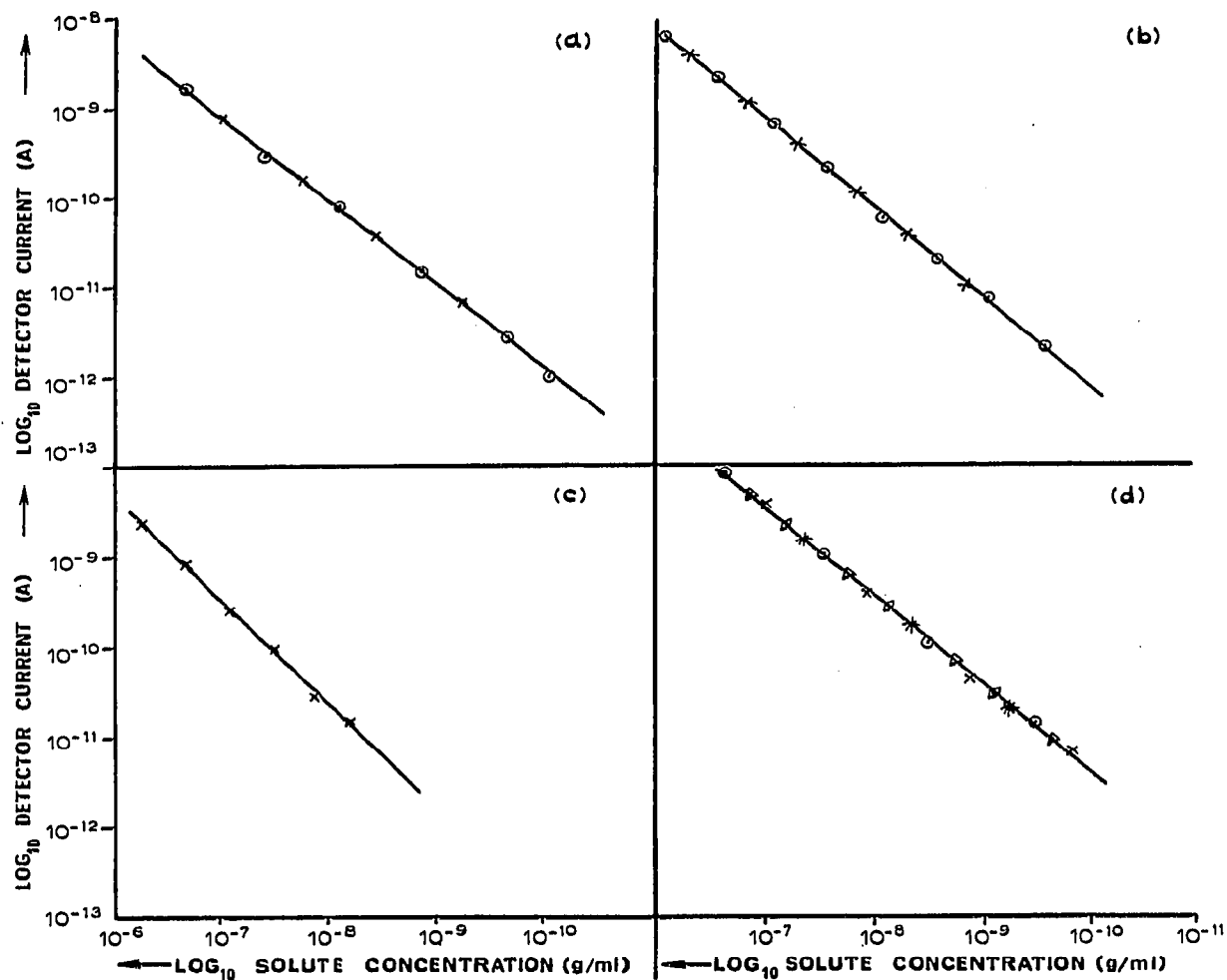


Fig. 3. Response curves for the flame ionisation detector for various flow-parameters and voltages. Detector temperature: 23° . Solute: (a), (b) and (c) diisopropyl ether; (d) *n*-heptane. Detector flow-rate: (a), (c) and (d) 60 ml/min; (b) 30 ml/min. Hydrogen flow-rate: (a), (b) and (d) 60 ml/min; (c) 90 ml/min. Oxygen flow-rate: 60 ml/min.

	Voltage	Minimum detectable signal (estimate) g/ml	Ionization efficiency %	Response index	Range g/ml	Noise level <i>A</i>
(a)	50	$6.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	0.96	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
	100	$6.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	0.96	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
(b)	50	$9.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	1.01	$10^{-6} - 5 \cdot 10^{-10}$	$8 \cdot 10^{-13}$
	100	$9.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$	1.01	$10^{-6} - 5 \cdot 10^{-10}$	$8 \cdot 10^{-13}$
(c)	100	$3.5 \cdot 10^{-10}$	$2.5 \cdot 10^{-4}$	1.13	$10^{-6} - 10^{-8}$	$8 \cdot 10^{-13}$
(d)	25	$1.8 \cdot 10^{-11}$	$4.0 \cdot 10^{-3}$	0.98	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
	50	$1.8 \cdot 10^{-11}$	$4.0 \cdot 10^{-3}$	0.98	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
	75	$1.8 \cdot 10^{-11}$	$4.0 \cdot 10^{-3}$	0.98	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
	100	$1.8 \cdot 10^{-11}$	$4.0 \cdot 10^{-3}$	0.98	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$
	150	$1.8 \cdot 10^{-11}$	$4.0 \cdot 10^{-3}$	0.98	$2 \cdot 10^{-7} - 10^{-10}$	$8 \cdot 10^{-13}$

The ionisation efficiency calculated for this detector compares favourably with that obtained by ONGKIEHONG⁴ and DESTY *et al.*², although the limit of its sensitivity is not as high as the values quoted by these authors. The lower sensitivity is probably due to the higher noise level of the ancillary equipment and not to the flame-ionisation detector itself. Results show that the flame ionisation detector is very satisfactory for quantitative gas chromatographic analysis. It is possible, however, to obtain higher sensitivity if one is prepared to accept a detector with a non-linear response.

Macro argon ionisation detector

A diagram of the detector is shown in Fig. 4. The detector is constructed of brass and contains a central cylindrical electrode that terminates in a small sphere. The electrode,

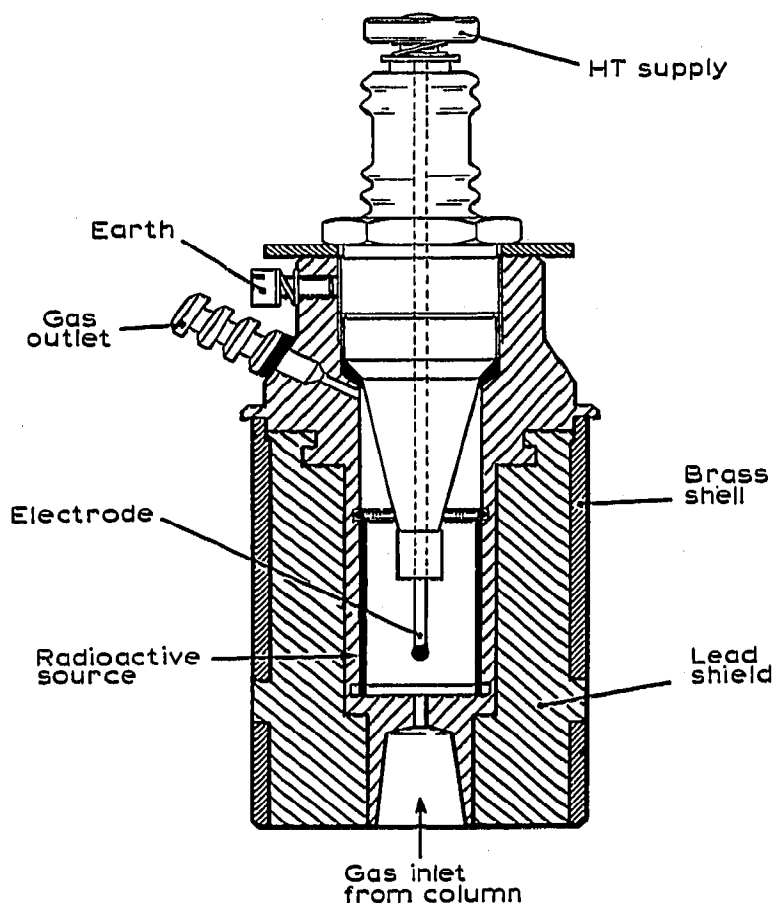


Fig. 4. Cross section of argon ionisation detector.

which is a modified sparking plug, is insulated from the body of the detector by means of a ceramic sleeve. A radioactive source (strontium-90) in the form of a foil is fitted concentric with the electrode.

The response of the detector was examined at various voltages and flow-rates with, and without, a linearizing resistance incorporated in the anode lead and at temperatures of 50° and 70°.

Results. In Figs. 5 and 6 the data obtained are presented as a graph of \log_{10} ionisation current against \log_{10} concentration. The absolute sensitivity, ionisation

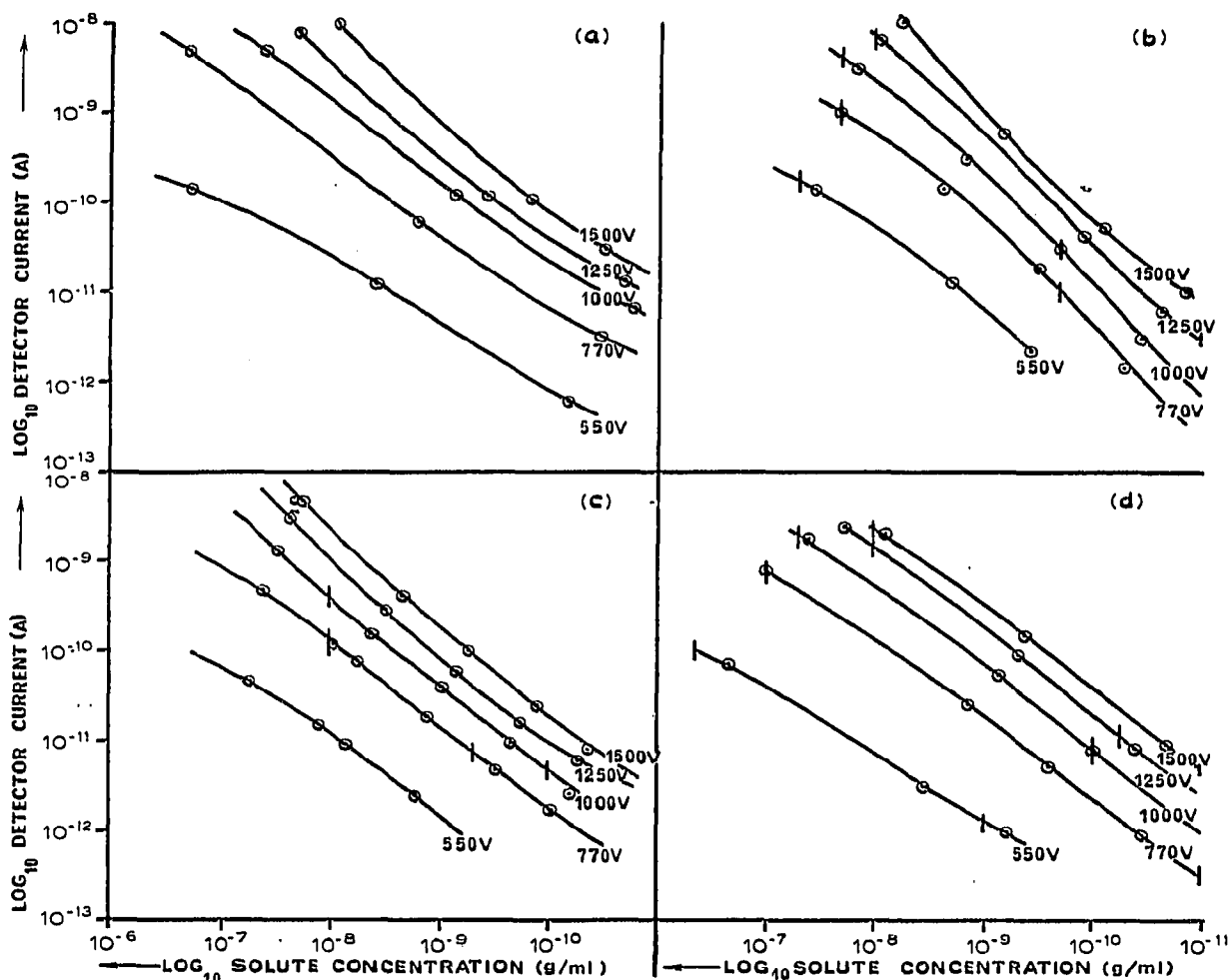


Fig. 5. Response curves for the argon ionisation detector for different solutes. With linearising resistance. Column flow-rate: 60 ml/min. Detector temperature: 75°. Solute: (a) toluene; (b) chlorobenzene; (c) *n*-heptane; (d) diisopropyl ether.

	Voltage	Minimum detectable signal (estimate) g/ml	Ionization efficiency %	Response index	Range g/ml	Noise level A
(a)	550	$6.5 \cdot 10^{-11}$	$4.7 \cdot 10^{-3}$			$6.0 \cdot 10^{-12}$
	770	$< 10^{-13}$	$4.2 \cdot 10^{-2}$			$3.0 \cdot 10^{-12}$
	1000	$< 10^{-13}$	$1.5 \cdot 10^{-1}$			$3.0 \cdot 10^{-12}$
	1250	$< 10^{-13}$	$3.4 \cdot 10^{-1}$			$3.6 \cdot 10^{-12}$
	1500	$< 10^{-13}$	$7.5 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(b)	550	$2.4 \cdot 10^{-11}$	$2.2 \cdot 10^{-2}$	0.91	$5 \cdot 10^{-8} - 5 \cdot 10^{-10}$	$6.0 \cdot 10^{-12}$
	770	$2.4 \cdot 10^{-12}$	$6.4 \cdot 10^{-2}$	0.95	$2 \cdot 10^{-8} - 2 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$8.5 \cdot 10^{-12}$	$2.3 \cdot 10^{-1}$	0.99	$2 \cdot 10^{-8} - 2 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$1.5 \cdot 10^{-13}$	$5.0 \cdot 10^{-1}$	1.51	$10^{-8} - 10^{-11}$	$3.6 \cdot 10^{-12}$
	1500	$2.0 \cdot 10^{-13}$	$9.4 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(c)	550	$4.2 \cdot 10^{-10}$	$1.1 \cdot 10^{-3}$			$6.0 \cdot 10^{-12}$
	770	$1.0 \cdot 10^{-11}$	$1.6 \cdot 10^{-2}$	0.95	$10^{-8} - 5 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$1.0 \cdot 10^{-12}$	$3.9 \cdot 10^{-2}$	0.93	$10^{-8} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$1.1 \cdot 10^{-13}$	$8.7 \cdot 10^{-2}$			$3.6 \cdot 10^{-12}$
	1500	$< 10^{-13}$	$1.8 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(d)	550	$3.2 \cdot 10^{-11}$	$1.4 \cdot 10^{-3}$	0.87	$5 \cdot 10^{-7} - 10^{-9}$	$6.0 \cdot 10^{-12}$
	770	$9.0 \cdot 10^{-12}$	$1.8 \cdot 10^{-2}$	0.92	$10^{-7} - 5 \cdot 10^{-11}$	$3.0 \cdot 10^{-12}$
	1000	$1.0 \cdot 10^{-13}$	$4.6 \cdot 10^{-2}$	0.89	$5 \cdot 10^{-8} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	10^{-13}	$8.3 \cdot 10^{-2}$	0.86	$10^{-8} - 5 \cdot 10^{-11}$	$3.6 \cdot 10^{-12}$
	1500	10^{-13}	$1.5 \cdot 10^{-1}$	0.88	$10^{-8} - 10^{-11}$	$6.0 \cdot 10^{-12}$

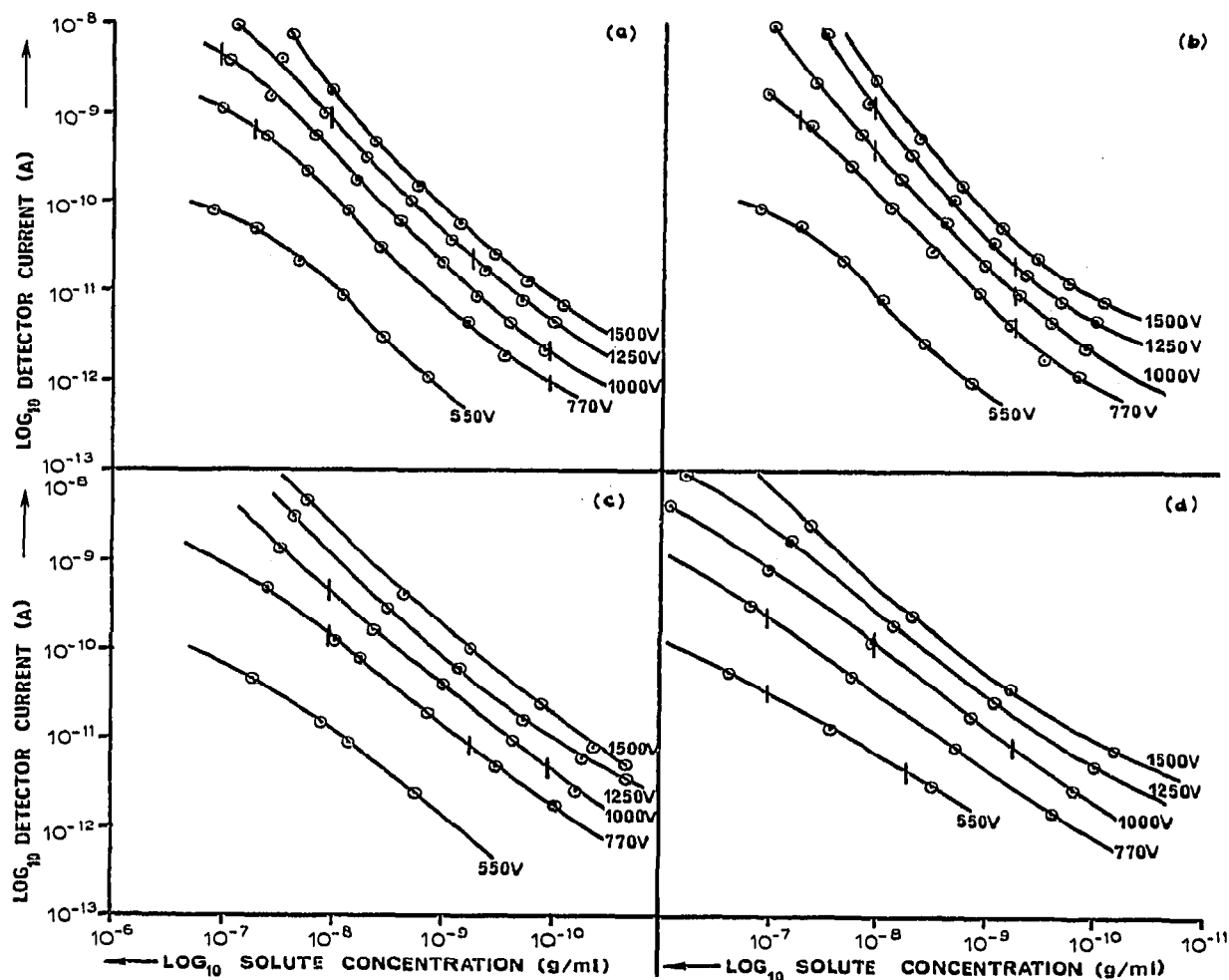


Fig. 6. Response curves for the argon ionisation detector at different flow-rates and temperatures. (a), (c) and (d) with linearising resistance; (b) without linearising resistance. Column flow-rate: (a) and (b) 30 ml/min; (c) and (d) 60 ml/min. Detector temperature: (a), (b) and (c) 75°; (d) 46°. Solute: *n*-heptane.

	Voltage	Minimum detectable signal (estimate) g/ml	Ionization efficiency %	Response index	Range g/ml	Noise level \bar{A}
(a)	550	$6.0 \cdot 10^{-10}$	$2.1 \cdot 10^{-3}$	1.11	$10^{-8} - 10^{-9}$	$6.0 \cdot 10^{-12}$
	770	$3.0 \cdot 10^{-11}$	$2.7 \cdot 10^{-2}$	1.14	$5 \cdot 10^{-8} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$9.0 \cdot 10^{-12}$	$6.9 \cdot 10^{-2}$	1.08	$10^{-7} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$1.0 \cdot 10^{-12}$	$1.7 \cdot 10^{-1}$	1.60	$10^{-8} - 5 \cdot 10^{-10}$	$3.6 \cdot 10^{-12}$
	1500	$1.0 \cdot 10^{-12}$	$3.7 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(b)	550	$7.5 \cdot 10^{-10}$	$2.3 \cdot 10^{-3}$			$6.0 \cdot 10^{-12}$
	770	$1.5 \cdot 10^{-11}$	$2.9 \cdot 10^{-2}$	1.26	$5 \cdot 10^{-7} - 5 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$5 \cdot 10^{-12}$	$8.3 \cdot 10^{-2}$	1.19	$10^{-8} - 5 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$1 \cdot 10^{-12}$	$2.0 \cdot 10^{-1}$	1.30	$10^{-8} - 5 \cdot 10^{-10}$	$3.6 \cdot 10^{-12}$
	1500	$< 10^{-13}$	$5.0 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(c)	550	$4.2 \cdot 10^{-10}$	$1.1 \cdot 10^{-3}$			$6.0 \cdot 10^{-12}$
	770	$1.0 \cdot 10^{-11}$	$1.6 \cdot 10^{-2}$	0.95	$10^{-8} - 5 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$1.0 \cdot 10^{-12}$	$3.9 \cdot 10^{-2}$	0.93	$10^{-8} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$1.1 \cdot 10^{-13}$	$8.7 \cdot 10^{-2}$			$3.6 \cdot 10^{-12}$
	1500	$< 10^{-13}$	$1.8 \cdot 10^{-1}$			$6.0 \cdot 10^{-12}$
(d)	550	$4.0 \cdot 10^{-10}$	$6.8 \cdot 10^{-4}$	0.81	$5 \cdot 10^{-7} - 5 \cdot 10^{-9}$	$6.0 \cdot 10^{-12}$
	770	$1.0 \cdot 10^{-11}$	$3.3 \cdot 10^{-3}$	0.89	$10^{-7} - 10^{-10}$	$3.0 \cdot 10^{-12}$
	1000	$2.0 \cdot 10^{-12}$	$1.1 \cdot 10^{-2}$	0.92	$10^{-8} - 5 \cdot 10^{-10}$	$3.0 \cdot 10^{-12}$
	1250	$4.0 \cdot 10^{-13}$	$2.8 \cdot 10^{-2}$			$3.6 \cdot 10^{-12}$
	1500	$4.1 \cdot 10^{-13}$	$5.7 \cdot 10^{-2}$			$6.0 \cdot 10^{-12}$

efficiencies and response indices for the four substances are also included in Fig. 5. The argon detector has a linear response for any given substance only over a small concentration range and at a particular voltage. Throughout the investigation a flame-ionisation detector was operated in series with the macro-argon detector and at all times it showed a linear response. Thus, any deviation from a linear response of the argon-ionisation detector was due solely to the detector and not to any part of the calibration system.

In Figs. 6(a) and 6(b) a comparison of response indices and concentration ranges for different voltages indicates that the use of a linearising resistance does not significantly improve the linearity of the detector. This fact has been substantiated by plotting detector current against voltage for different concentrations of *n*-heptane, with and without a linearising resistance (see Fig. 7).

In view of the capacity for chlorinated hydrocarbons to undergo electron capture, it is surprising to see, from Fig. 5 (b), that the argon detector has an approximately linear response over the concentration range 10^{-8} to 10^{-10} g/ml for chlorobenzene when operated at 770 and 1000 V.

Since the response indices for the four substances are generally outside those

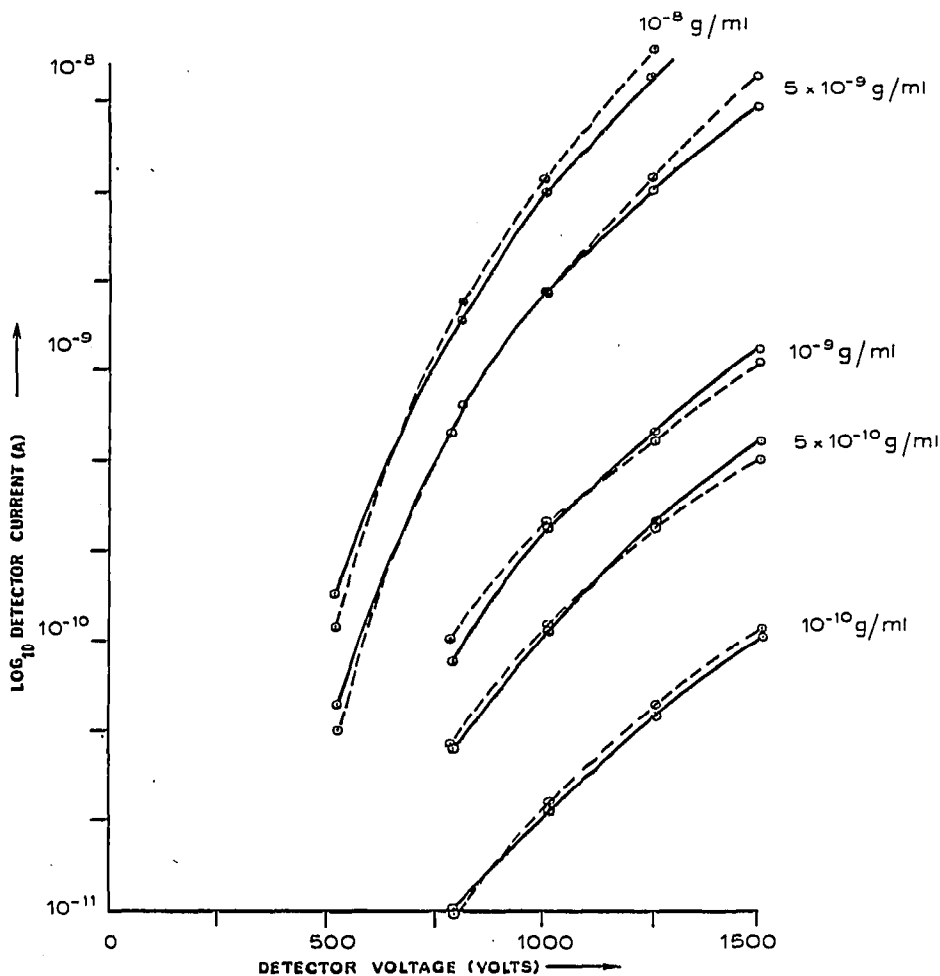


Fig. 7. Variation of ionisation current with voltage at different solute concentrations for the argon ionisation detector. With linearising resistance: ———. Without linearising resistance: - - -. Column flow-rate: 30 ml/min. Detector temperature: 75° . Solute: *n*-heptane.

acceptable for any detector in quantitative analysis, calibration of the macro-argon detector is therefore necessary for each compound at each particular voltage.

Figs. 6a, 6c and 6d show that increases in temperature and flow-rate improve the response index of the detector for *n*-heptane.

The maximum sensitivity for all four components studied was of the order of 10^{-13} g/ml. Where maximum sensitivity is required the argon detector can be advantageously used, but when quantitative results are necessary with the minimum of calibration then the flame-ionization detector should be employed.

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SUMMARY

The flame-ionisation detector has a linear response over a range of four orders of concentration, *i.e.* 10^{-6} to 10^{-10} g/ml, and this range could probably be extended to six orders by employing suitable experimental conditions. The detector response is independent of the applied voltage, over the range of 25–150 V, and has a sensitivity of approximately 10^{-11} g/ml.

The macro-argon ionisation detector has a linear response over a small concentration range at one particular voltage, the value of which may vary from one substance to another. Inclusion of a linearising resistance does not result in a linear response. Calibration of the macro-argon detector is essential for accurate quantitative analysis due to the variability of the response index. The sensitivity of the detector is about 10^{-13} g/ml.

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