LINEARITY AND RESPONSE CHARACTERISTICS OF THE FLAME IONISATION DETECTOR

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INTRODUCTION

The application of gas chromatography to the analysis of both major and minor components in a sample requires either a detector of high sensitivity and wide response range or a system involving either sample splitting or preconcentration techniques. A high sensitivity detector is more rapid and much simpler. If, however, such a detector is used, it is necessary to know whether its response is strictly linear over the required range. Most detectors are linear over a range of less than 10^4 to 1. Recent reports[1-4] on the linearity of the flame ionisation detector[5,6] have indicated a linear range of 10^7 to 1 and up to 0.5 % constituent in the gas stream. As part of a study of the response characteristics of this detector, its upper linear range and optimum operating conditions have been investigated in some detail at the ICIANZ Central Research Laboratories.

APPARATUS

The detector construction was similar to that described previously[5], but using a single jet and an electrical bias to offset the background current at high sensitivity. A single valve (ME1403) impedance conversion circuit with a gain of 1/15 and grid input resistors of 10^5-10^{11} ohms were used. Gas flow rates were measured in terms of the pressure drop (5–35 p.s.i.g.) across glass capillaries calibrated with a soap film or moving bubble flow meter. The air flow rate in the 9 cm diameter combustion chamber (containing two jets) was approximately 1 litre/min, and the data shown were obtained with a flat probe (upper) electrode consisting of a 1.5 cm square of approximately 25 mesh BSS brass gauze and a jet made from 20 gauge hypodermic needle tubing.

RESULTS AND DISCUSSION

Effect of applied voltage

The detector output for a given gas concentration increeces with the voltage applied between the probe electrode and the jet until a plateau is reached. It is assumed that the plateau corresponds to collection of all ions formed in the flame. For an impurity flow rate of 50 μg/sec and a probe to jet distance of 5 mm (see below) the plateau was

reached in this investigation at approximately 360 V and extended at least to above 900 V. For lower amounts of impurities, *i.e.* smaller number of ions, lower voltages are adequate as shown in Fig. 1. This effect is due partly to greater ion recombination at high concentrations and partly to space charge effects. It is seen that a considerably lower voltage can be used on equipment designed solely for work with capillary columns[3,7] than for general purpose units for use with granular packed columns and larger samples.

At low concentrations a positive probe electrode gives superior ion collection efficiency to a negative probe, as would be expected from the higher mobility of electrons compared with positive ions. However, at higher concentrations, provided that the probe–jet gap is not too large, better results are obtained with a negative probe (see Fig. 1).

Effect of probe to jet distance

If a flat probe electrode is used, the efficiency of ion collection is markedly influenced by the distance between the probe electrode and the tip of the flame jet. Examples of this effect are given in Figs. 1, 2 and 3. Fig. 2 shows that at higher concentrations the
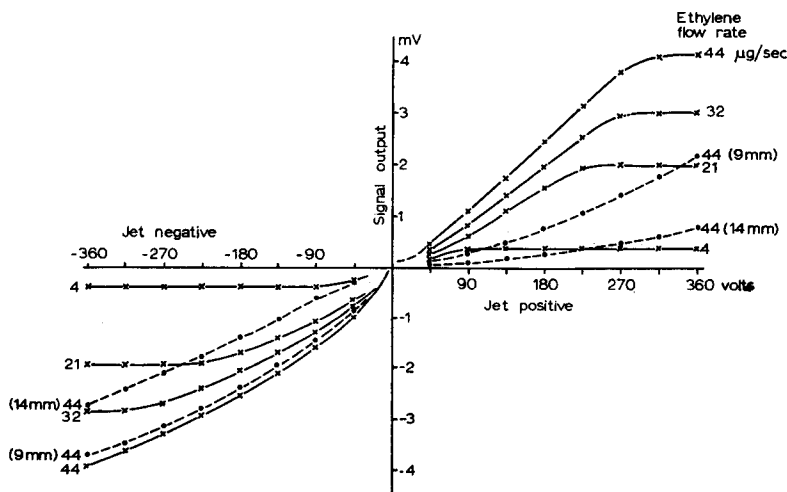

Fig. 1. Effect of probe–jet voltage on ion collection efficiency (grid resistor $1 \times 10^5 \Omega$ nominal, nitrogen flow rate 38 ml/min, hydrogen flow rate 38 ml/min, probe–jet distance 5 mm or as stated).

probe–jet distance is very critical if linearity is to be obtained, while Fig. 3 indicates that even at the lower concentrations a very wide gap should be avoided. A hat-shaped collector electrode consisting of a flat upper section and a cylinder surrounding the flame, so that a large solid angle is subtended at the jet by the probe electrode, gives results similar to the small probe–jet gap without overheating the probe electrode.
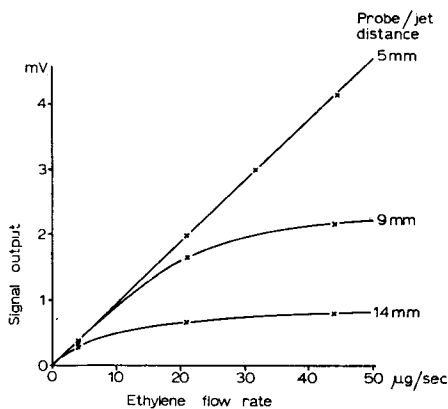
Fig. 2. Effect of probe–jet distance on linearity (conditions as for Fig. 1, probe–jet voltage 360 V jet positive).
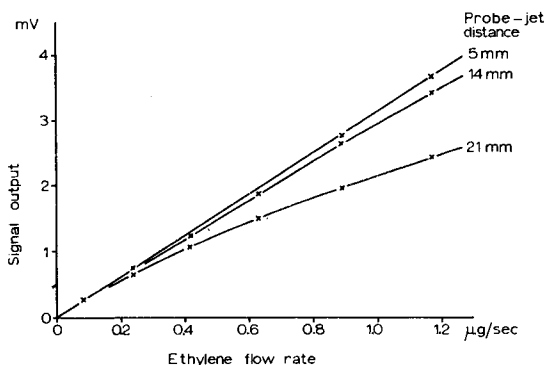

Fig. 3. Effect of probe–jet distance on linearity (grid resistor $3 \times 10^6 \Omega$ nominal, other conditions as for Fig. 2).

Effect of nitrogen and hydrogen flow rates

The effect on the signal output of the detector of changing the nitrogen and hydrogen flow rates (at a fixed sample flow rate) is shown in Fig. 4. As mentioned previously[5], for each value of the nitrogen flow rate there exists a corresponding hydrogen flow rate at which a maximum signal output is obtained. The optimum nitrogen : hydrogen ratios for various nitrogen flow rates have been plotted in Fig. 5, and it is seen that in this case the optimum ratios approach a constant value of 1.5 as the flow rates increase.

The optimum signal output conditions appear to correspond to those for the maximum signal to noise ratio of the detector. However, at any fixed nitrogen flow rate, as the hydrogen flow rate is increased past the optimum value, the signal not only decreases but the total background appears to increase almost exponentially. For this reason, and since the change in background ion current with change in nitrogen or hydrogen flow is dependent on the nitrogen and hydrogen impurity concentrations under non-optimum flow conditions (see Fig. 4), ultimate sensitivity determinations by the hydrogen addition method used by ONGKIEHONG[2] must be done under optimum flow conditions. The difference between the optimum ratio found in this study and that reported by CONDON, SCHOLLY AND AVERILL[1] is presumably due to their use of a

thick-walled jet to serve as a heat sink, since the ratio appears to be relatively independent of the internal diameter of the jet.

Examination of Fig. 4 shows that the linearity of response is maintained for all nitrogen and hydrogen flow rates under conditions of efficient ion collection. It should
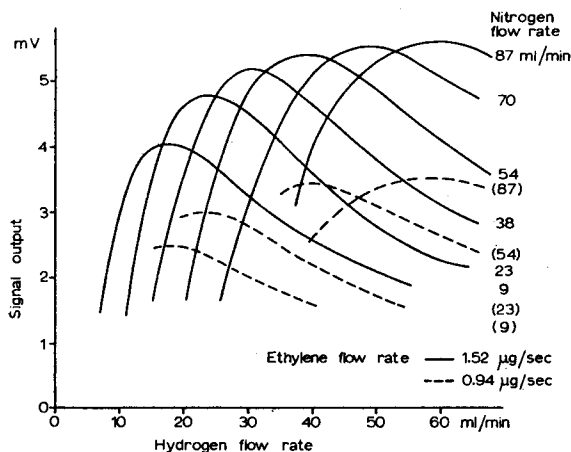

Fig. 4. Effect of hydrogen and nitrogen flow rates on ion formation, (conditions as for Fig. 3 with probe–jet distance 5 mm).

also be noted that when operated at the optimum nitrogen : hydrogen ratio, small changes in the hydrogen, nitrogen or total flow rate have little effect on the signal output of the detector.

According to the response curves given here and the background noise limit given by KIESELBACH[4], the sensitivity limit of the detector is better than 3.10^{-7} μg/sec, and the response therefore covers a range of over 10^8 to 1 up to 5 % v/v at the detector (10 % in the nitrogen carrier gas stream). The results of this investigation and that
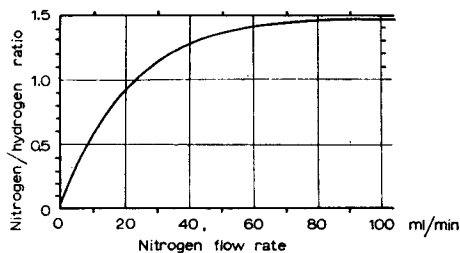

Fig. 5. Optimum nitrogen: hydrogen ratios.

reported by DESTY, GEACH AND GOLDUP[3] show strict linearity over the range from 50 μg/sec down to 3.10^{-4} μg/sec, a ratio of over 10^5 to 1.

The above data also show that the detector can be used in the medium sensitivity range for hydrogen, nitrogen and materials to which it does not normally respond. This is done by using a large hydrogen flow rate to give an initially high background signal[8] or by bleeding in a constant stream of, e.g., coal gas and operating at a non-optimum nitrogen : hydrogen ratio.

Abnormal non-linearity effects

It is generally considered that the flame ionisation detector is relatively insensitive to inorganic gases, including carbon disulphide. However, in the latter case it has been found that an initial sensitive response is obtained which is quickly suppressed at higher concentrations, resulting in peak inversion as shown in Fig. 6, which was obtained with a 0.02 in. capillary column. This behaviour appears to be peculiar to carbon disulphide as it has not so far been observed with any other material using the present electrode system. It was initially believed that the effect was due simply
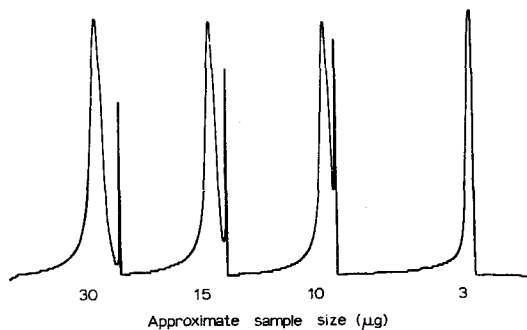

Fig. 6. Response of carbon disulphide.

to inhibition of ion formation by the products of combustion. However, addition of sulphur dioxide (or hydrogen sulphide) to coal gas which was then fed directly to the detector did not inhibit the signal due to the coal gas alone.

NOVÁK AND JANÁK[13] have reported peak inversion effects with hydrocarbons at concentrations of about 8 μg/sec (0.65 % by volume), which is to be compared with the peak concentration of carbon disulphide in this case of 0.4 μg/sec (0.03 % by volume). However, they showed that their results were due to the design of their electrode system which would be expected to produce non-linear effects.

Use of non-linear response

Although a strictly linear detector response is desirable for many applications, the analysis of wide range samples may involve a large number of sensitivity changes. Range extension by automatic offset without change in sensitivity is unsatisfactory due to the greatly increased recorder balancing time. Extension of range by automatic sensitivity changes also causes some loss in recording speed, and the resulting chromatogram is untidy and difficult to follow. This can be avoided by the use of a logarithmic or other non-linear scale. By feeding the signal to the recorder via a suitably loaded multitap potentiometer geared to the recorder balancing motor an almost true logarithmic response can be obtained[9]. An alternative quasi-logarithmic response system is described below which is applicable to any high-impedance ionisation detector.

Under normal conditions of operation of the flame ionisation detector the current flowing round the circuit shown in Fig. 7 is determined by the effective flame resist-

tance, R, and the battery voltage, V, the grid input resistor, r, being much less than R. If, however, the grid input resistor is comparable with the flame resistance, the voltage drop across r is given by $v = rV/(r+R)$. From this function the relation between v/V and r/R is plotted on a semi-logarithmic scale in Fig. 8. For constant V and r, the
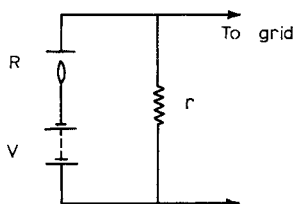

Fig. 7. Basic circuit of flame ionisation detector.

signal output over the middle of the range shown in Fig. 8 is almost linearly proportional to log (r/R) which is proportional to log (flame conductivity) and hence to log (sample concentration). The response is linear in the high sensitivity region, logarithmic in the intermediate region, and tends to a limiting value at large sample sizes. It should be noted that the baseline reading represents the total background current in the flame circuit. In practice the low-sensitivity end of the response curve will differ somewhat from that shown in Fig. 8 since no allowance has been made for the
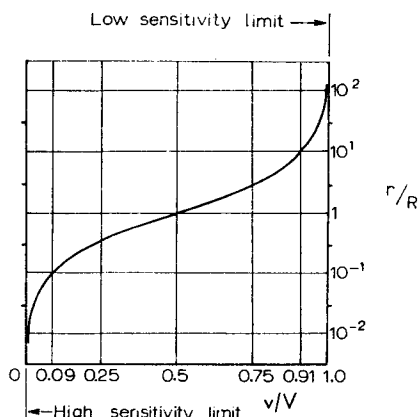

Fig. 8. Non-linear response curve.

variation of resistance with applied voltage[10] of the high-value resistor, r, nor for the reduction in voltage across the flame which may affect the ion collection efficiency as discussed in the previous sections.

Mechanism of ion formation

The abnormally high degree of ionisation in a hydrocarbon flame cannot be simply accounted for on the basis of the thermal ionisation of hydrocarbon molecules (which have ionisation potentials in the region of 9–12 eV). A possible mechanism of ion

formation based on the formation of carbon aggregates and their subsequent thermal ionisation has been suggested[11], and a recent investigation of the flame ionisation detector has been regarded as supporting this view since the number of molecules required to produce one ion is roughly equal to the number of carbon atoms required to form suitably sized aggregates[2]. An alternative and more likely explanation, however, is possible.

It is supposed that due to the reactions occurring in the flame an intermediate "reaction complex" is formed with one of the carbon atoms in the molecule. The complex so formed will exist in an entirely different (excited) electronic and vibrational state from that of the parent hydrocarbon. Subsequent thermal ionisation of this complex may therefore occur with a relatively high probability since the limitation imposed by the normally high ionisation potential of the parent molecule is removed. A linear detector response can be expected from such a mechanism, and the proportionality of the response per mole to the number of carbon atoms in the molecule[1-3,5] is explained by the proportionately larger number of centres at which reaction may be initiated. Assuming further that carbon–oxygen attachment prior to formation of carbon dioxide is the critical step, the insensitivity of carbon monoxide and carbon dioxide is explained and also the lower sensitivity of oxygen-containing molecules compared with the corresponding hydrocarbons.

Formation of (hydrated) hydrogen ions as part of the basic ion formation mechanism, suggested by mass spectrometric studies[12], appears to be unlikely due to the sensitive response obtained with carbon tetrachloride.

SUMMARY

Non-linearity of the flame ionisation detector at high concentrations has been shown to be caused by inefficient ion collection, due to ion recombination and space charge effects, rather than a basic non-linearity of ion formation. This can be overcome by using a flat probe electrode which subtends a large angle at the jet or a hat-shaped collector in conjunction with an adequate probe–jet voltage. With a detector unit similar to that described previously[5,6] a linear response up to 10 % sample in the nitrogen carrier gas stream (5 % at the jet) has been obtained (50 μg/sec at 25 ml/min nitrogen). A non-linear response system to avoid sensitivity changes with wide range samples is described. A possible explanation of the abnormally high degree of ionisation found in hydrocarbon flames is suggested.

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