OPERATIONAL MECHANISM AND PERFORMANCE OF A SUBSIDIARY DISCHARGE ARGON IONIZATION DETECTOR

MIKIYA YAMANE

Hitachi Central Research Laboratory, Kokubunji, Tokyo (Japan)

(Received October 25th, 1962)

It has been shown in a work[1] previously reported that a subsidiary discharge argon ionization detector in conjunction with an electrometer of high gain can be used to measure the amounts of components present in the effluent of a gas chromatographic column. The principle of operation of the detector, *i.e.* the mechanism of ionization of the sample, might be regarded as the same as that of LOVELOCK's detector[2], but it has an outstanding feature in that the radioactive source is replaced by a D.C. subsidiary discharge. The detector, consisting of a concentric diode with discharge electrodes mounted in the scavenging gas flow (discharge gas flow), was said to operate in such a way that primary electrons generated by the discharge were carried into the sensing chamber by the flow of the discharge gas. A complete description of this mechanism was not given in the previous paper, however, and the way in which primary electrons are generated was not at all well understood. The primary purpose of this work was to obtain more information on this aspect of the device.

It is known that the limiting noise in an argon ionization detector is determined by the uniformity with which primary electrons are generated. Therefore, in this detector the steadiness of the subsidiary discharge is of great importance. In the previous paper attention was drawn to the fact that the same arrangement could give more satisfactory operation if helium were used as the discharge gas. The use of helium permits a relatively low voltage breakdown to be started and a steady low-noise discharge to be maintained at atmospheric pressure.

The present investigation was conducted with a glass-housed detector of small volume, helium being used as the discharge gas and argon as the carrier gas. As a preliminary test, the discharge in the helium flow was studied with a simple discharge tube to prove its suitability as an electron source. Next, the characteristics of the background current were investigated in detail with a view to clarifying the generation mechanism of primary electrons. Finally, the response of the detector was tested. The performance studies proved to be quite satisfactory. The results of these measurements, together with a discussion of these experimental results, are given in the present paper.

APPARATUS

The experimental setup, which is shown in Fig. 1, is similar to the arrangement already described in the previous paper. The only significant difference is the incorporation of a helium flow line, so that the discharge may be excited in pure helium flow. Argon is used as the carrier gas, in order to maintain the high sensitivity of the argon

ionization detector. The two gases are supplied from normal commercial cylinders, and the purities are both listed as being above 99.9 %.

The most important part of the apparatus is the detector, of which the electrode geometry must be carefully chosen, if good signal-to-noise performance is to be

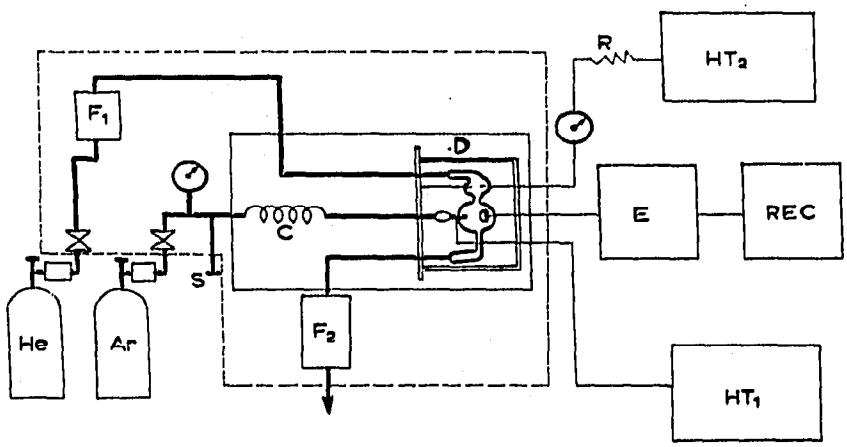

Fig. 1. Diagram of apparatus. Ar = argon cylinder; He = helium cylinder; F_1, F_2 = flow meters; S = sample introducing device; C = column; D = detector; HT_1 = high voltage supply for the detector; HT_2 = high voltage supply for the discharge; R = current limiting resistor; E = electrometer amplifier; REC = recorder.

realized. The detector used in this investigation is shown schematically in Fig. 2. It consists of two chambers: one of which is the discharge chamber and the other the sensing chamber. The discharge chamber is made of a glass tube with an O.D. of 10 mm and a length of about 20 mm, into which is mounted a pair of 0.5 mm Kovar wires, the electrodes for the subsidiary discharge. The ends of the electrodes are bent towards each other, so that a steady discharge may be fixed there. Helium is led through a Kovar spring pipe (1.5 mm O.D. and 1 mm I.D.) into the discharge chamber, whence it flows into the sensing chamber through a narrow passage. The sensing chamber is also made of a 20 mm O.D. spherical glass tube. The inlet for the effluent gas, which acts as an anode, is made of a Kovar tube with an O.D. of 1.5 mm, an I.D. of

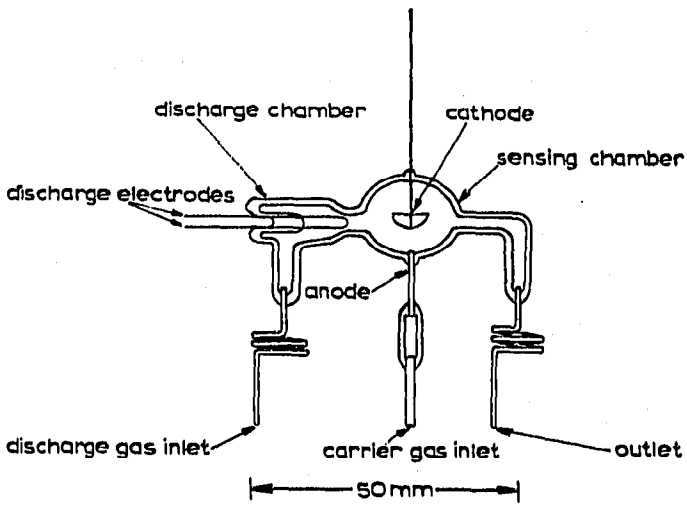

Fig. 2. Subsidiary discharge argon ionization detector.

1 mm and a length of 15 mm. The cathode is a semi-spherical nickel dish, and is located at the center of the sensing chamber.

EXPERIMENTAL RESULTS AND DISCUSSION

Subsidiary discharge

Many experimenters have studied the electrical discharge of helium at various pressures and in various different geometrical arrangements[3]. Since most workers have obtained data for pure helium with seal-off tubes, much of the available data cannot be applied to the actual operation of the detector, where the handling of helium from commercial cylinders can introduce small quantities of impurities, and occasional exposure to the air may change the surface condition of the electrodes.

A preliminary investigation on the characteristics of the subsidiary discharge in the flow of helium was made, using a discharge tube shown in Fig. 3. Electrodes of

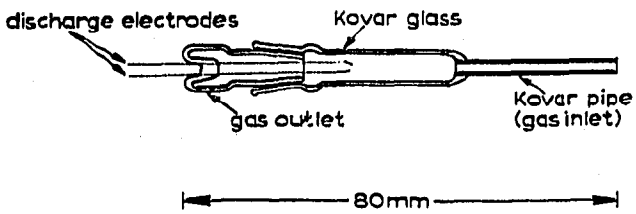

Fig. 3. Discharge tube.

0.5 mm Kovar wires were mounted, and made to be demountable from the tube by means of a ground glass joint, so that the spacing between the electrodes could be varied. The spacing was measured at an accuracy of about 0.01 mm with an optical projector.

In Fig. 4 is shown the breakdown voltage V_s plotted against the electrode spacing d. The curve represents the average of many series of measurement. The maximum breakdown voltage was usually obtained in the first run, and after the first breakdown was passed, V_s assumed a value which was appreciably less than the first one, and as the measurements were repeated, it decreased slightly. This gradual decrease is probably due to the cleaning up of the electrodes. The spread in the breakdown voltage, however, was less than about 50 V.

The results of the second investigation, designed to obtain the relation between the discharge current i_d and the maintaining voltage V_m, are shown in Fig. 5. The curves obtained at various gap distances all exhibit constant voltage characteristics. In view of the fact that the noise current to the sensing electrode depends on the stability of the discharge, such a constant voltage characteristic necessitates a stabilized voltage supply. The fluctuation of the discharge current Δi due to the instability of the voltage supply is given by $\Delta i = \Delta V/R$, where R is the current limiting resistance in the discharge circuit.

Background current

(*a*) *Effect of the polarity of voltage supply for the discharge.* Fig. 6 shows the typical background current curve which was obtained with a circuit shown in the inset

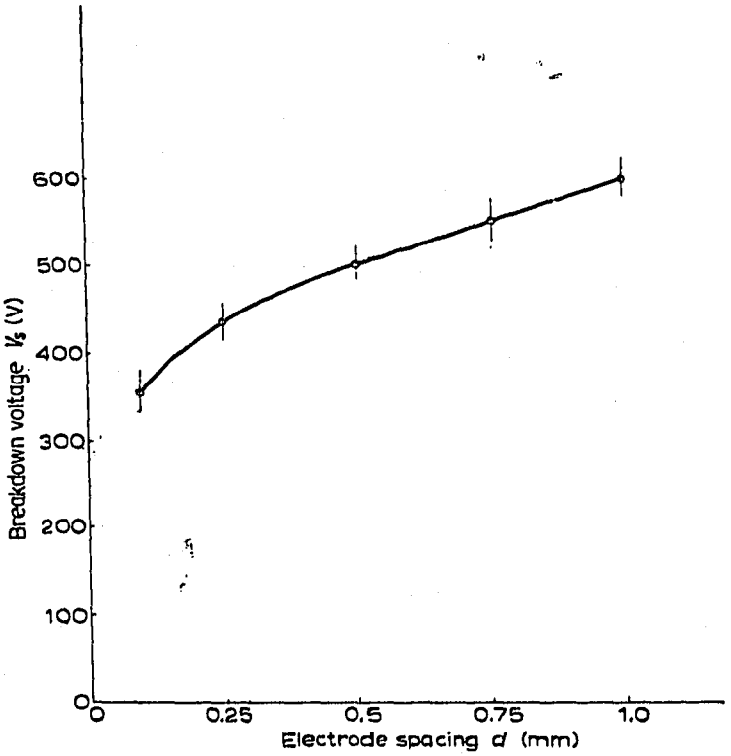

Fig. 4. Breakdown voltage in the helium flow as a function of electrode spacing.

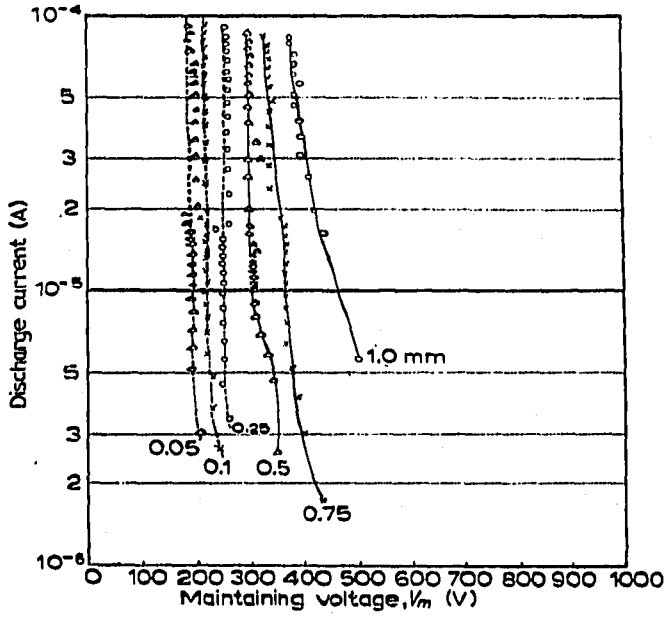

Fig. 5. Current–voltage characteristics of the discharge in the helium flow at different electrode spacings.

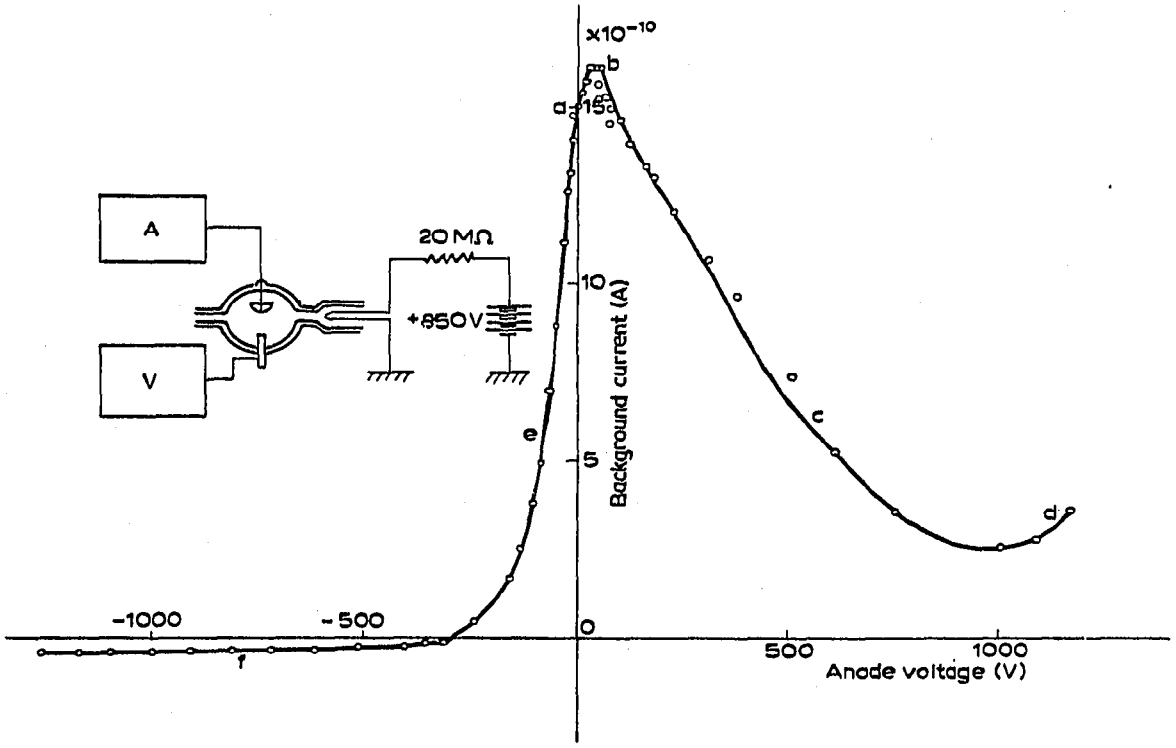

Fig. 6. Typical background current as a function of anode voltage, discharge being excited by a positive high voltage supply. Helium flow = 60 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

figure of Fig. 6. It should be noted here that the subsidiary discharge is excited by a positive high voltage supply. Measurement was made under the following conditions:

Argon carrier gas: 60 ml/min
Helium discharge gas: 60 ml/min
Discharge current: 30 μA

The curve exhibits a rather complicated shape: at negative high anode voltages a weak electron current flows to the cathode, and as the anode voltage is increased, there is a steep rise at voltages ranging from —200 V to 50 V with a maximum at 50 V, followed by a decline at higher anode voltages. It is now essential to offer some physical explanation for these characteristics. The explanation is, however, not too difficult, as will be apparent later.

In Fig. 7 is shown the background current to the cathode which was measured with a circuit shown in the inset figure of Fig. 7. In this case, the subsidiary discharge was excited by a negative high voltage supply. It can be seen that, although the other operational conditions are exactly the same as those mentioned above, the curve is very different from that of Fig. 6; it has such a shape as would be described if the curve of Fig. 6 were turned around the origin by 180°. This difference can be ascribed to the polarity of the high voltage supply for the discharge, and it is clear that the background current depends on the potential of the discharge chamber referred to that of the sensing chamber. An interpretation of the trend of the curves of Fig. 6 and Fig. 7, which, at the same time, explains the operational mechanism of this detector, is offered below.

(1) In the first case, when the discharge is excited by a positive high voltage supply (Fig. 6), the potential of the discharge chamber is positive because one electrode is at the earth potential and the other at about 250 V. When the anode voltage is 0 V, the potential of the sensing chamber is the earth potential and is negative with

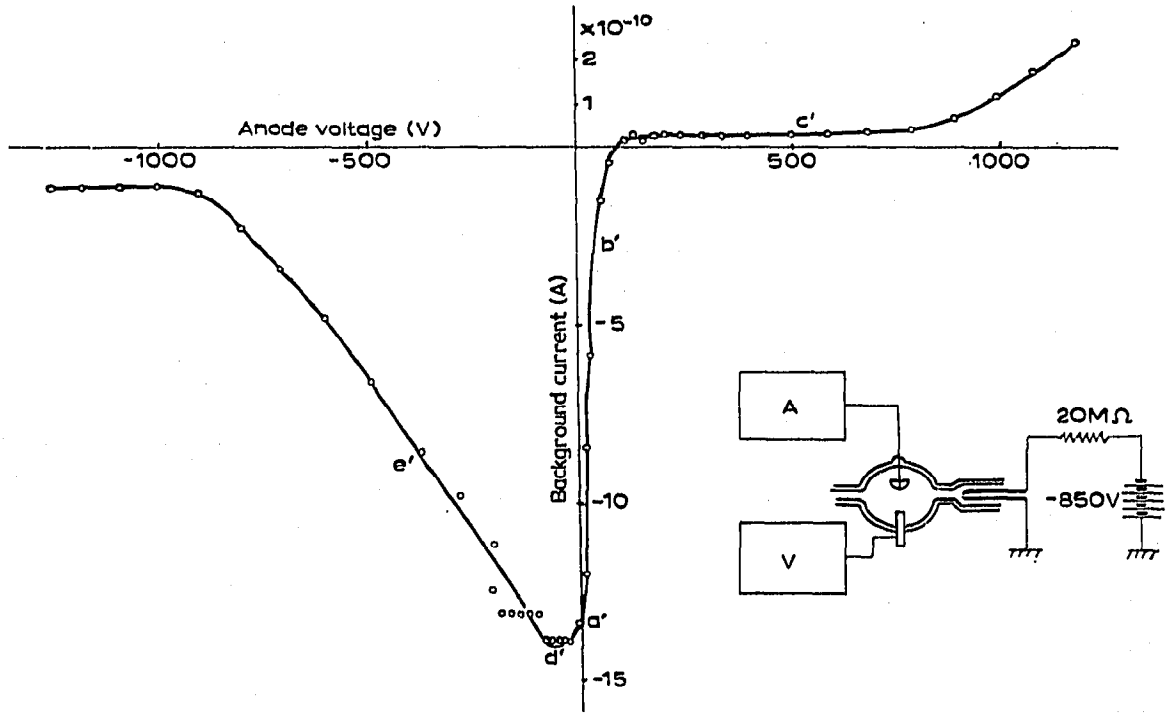

Fig. 7. Typical background current as a function of anode voltage, discharge being excited by a negative high voltage supply. Helium flow = 60 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

respect to that of the discharge chamber. Thus, ions produced by the discharge are drawn to the sensing chamber by an electrical force acting between the two chambers. These ions are captured by both the anode and the cathode, so that positive current is read by the electrometer (point a in Fig. 6). When the anode voltage is 50 V, positive ions are still drawn to the sensing chamber, but, repelled by the anode, most of them are collected by the cathode. At this voltage maximum ion current is measured by the electrometer (point b in Fig. 6). As the anode voltage is increased further, the potential of the sensing chamber rises, which starts inhibiting the flow of positive ions from the discharge and pulling out electrons gradually. This accounts for the negative characteristics of the curve (point c in Fig. 6). At voltages higher than 1000 V, ionization by collision of electrons sets in, thus again giving rise to an increase in the background current (point d in Fig. 6).

Next, let us analyze the current curve in the region below 0 V. When we apply negative voltage to the anode, the potential of the sensing chamber becomes negative, causing many positive ions to be drawn to the sensing chamber. Since most of these ions are collected by the anode, the share taken by the cathode is reduced, resulting in a decrease in the background current (point e in Fig. 6). In the region below —300 V, a small amount of saturated negative current is observed, which indicates that there is a flow of electrons to the cathode. Perhaps these electrons are produced

by photoionization, because at these anode voltages it is less likely for electrons to enter the sensing chamber from the discharge (point f in Fig. 6).

(2) When the discharge is excited by a negative high voltage supply (Fig. 7), the potential of the discharge chamber is negative. If the anode voltage is 0 V, the potential of the sensing chamber is the earth potential and positive with respect to that of the discharge chamber. This condition is favourable for electrons to be drawn to the sensing chamber by the electric field between the two chambers. Electrons thus drawn to the sensing chamber are captured by both the anode and the cathode. Thus, negative current is read by the electrometer (point a′ in Fig. 7). As the anode voltage is increased, more electrons are drawn to the sensing chamber. However, with a larger share of these electrons taken up by the anode, the electron current to the cathode decreases (point b′ in Fig. 7). At higher anode voltages a small amount of saturated positive ion current is seen to flow to the cathode. It appears that this positive current may be ascribed to photoionization within the sensing chamber. It should be noted here that the potential of the sensing chamber is now so highly positive with respect to that of the discharge chamber that a larger electron current flows to the anode (point c′ in Fig. 7).

When we apply negative voltage to the anode, the minimum background current is obtained at —50 V. The reason for this is that electrons still drawn to the sensing chamber are all collected by the cathode (point d′ in Fig. 7). Further increase in the negative value of the anode voltage causes the potential of the sensing chamber to be lowered, which starts inhibiting the flow of electrons to the sensing chamber. This, in turn, results in a gradual reduction in the electron current to the cathode (point e′ in Fig. 7).

Now it can be concluded from the qualitative considerations above that the background current to the cathode is predominantly due to the transfer of charged particles between the two chambers. It is clear that charged particles also flow to the anode, and of these particles the electrons are effective in ionizing sample gases. Therefore, it can be predicted that under the operational condition of c′ of Fig. 7, where an abundant supply of electrons is available in spite of the low background current, an advantageous performance of the detector may be realized.

(*b*) *Effect of the circuit condition of the discharge.* The presentation of the data which follows is mainly for the purpose of confirming the preceding considerations and illustrating a more effective way to use the detector. As stated earlier, the transfer of charged particles between the two chambers is dependent upon the potential of the discharge chamber relative to that of the sensing chamber. Since an abundant supply of free electrons would give an increased efficiency in actual practice, it would definitely be more satisfying if the discharge could be fired in such a manner that its potential becomes highly negative with respect to that of the sensing chamber. Such an adjustment of the discharge potential is easily achieved by a simple modification of the discharge circuit, *e.g.* by changing the position of the current limiting resistor in the circuit.

Fig. 8 illustrates the effect of the potential drop across the resistor on the background current. Measurements were made by exciting a discharge by a negative high voltage supply and with circuits shown in the inset figures of Fig. 8. The result of these measurements is what might be expected: lowering the discharge potential by the drop across the resistor causes many more electrons to be drawn to the sensing

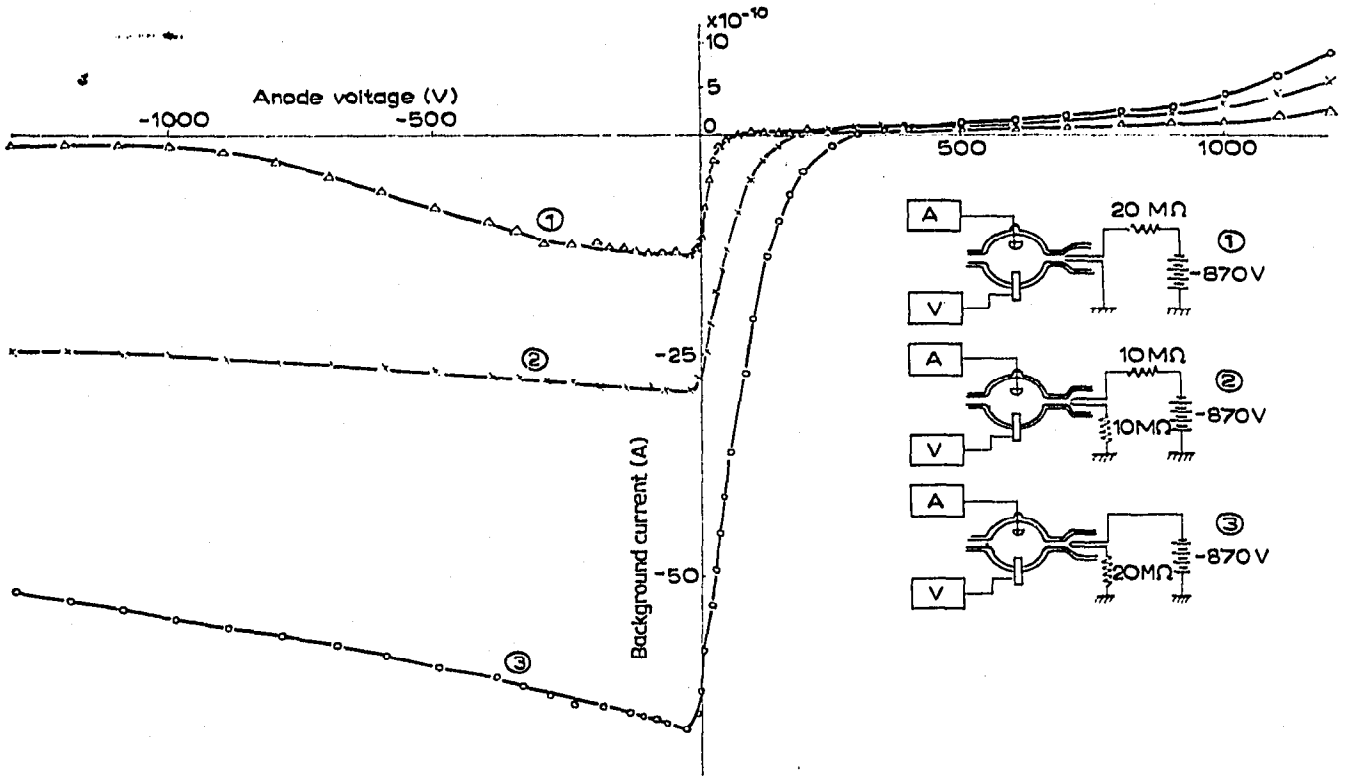

Fig. 8. Dependence of the background current upon the circuit condition of the discharge. Helium flow = 60 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

chamber, as illustrated by an increased electron current in the region of negative anode voltages. It is seen, moreover, that positive background current at positive anode voltages, which may be attributable to photoionization, is much less than the electron current, independent of the modification of the circuit. The control of the detector by the circuit modification is one of the particular advantages of this system.

(*c*) *Effect of the geometrical arrangement of the electrodes.* Thus far, we have dealt primarily with the mechanism by which primary electrons (background current) are generated, and made clear that the electrical force plays a predominant role. This fact leads us at once to the belief that the character of the detector must be governed to a great extent by the geometrical configuration of the electrodes, particularly by the position of the discharge electrodes relative to the sensing chamber.

Fig. 9 shows the background current for three different values of the anode position, the cathode being fixed at the center of the sensing chamber. It can be seen that the curves show no pronounced difference except that the slope marked b′ becomes less steep for a detector with widely spaced internal electrodes. Of importance in this study is the anode voltage at which the cathode collects zero net background current from the discharge. An advantage of operation at this point is that the input resistor of the electrometer (input sensitivity) can be switched without any noticeable shift in the baseline of the chromatogram.

In Fig. 10 are shown the background currents illustrating the effect of the position of the discharge electrodes relative to the sensing chamber. As would be expected, the intensity varies to a great extent with their position: it is easy to provide an abundant electron current, say in excess of 10^{-8} A.

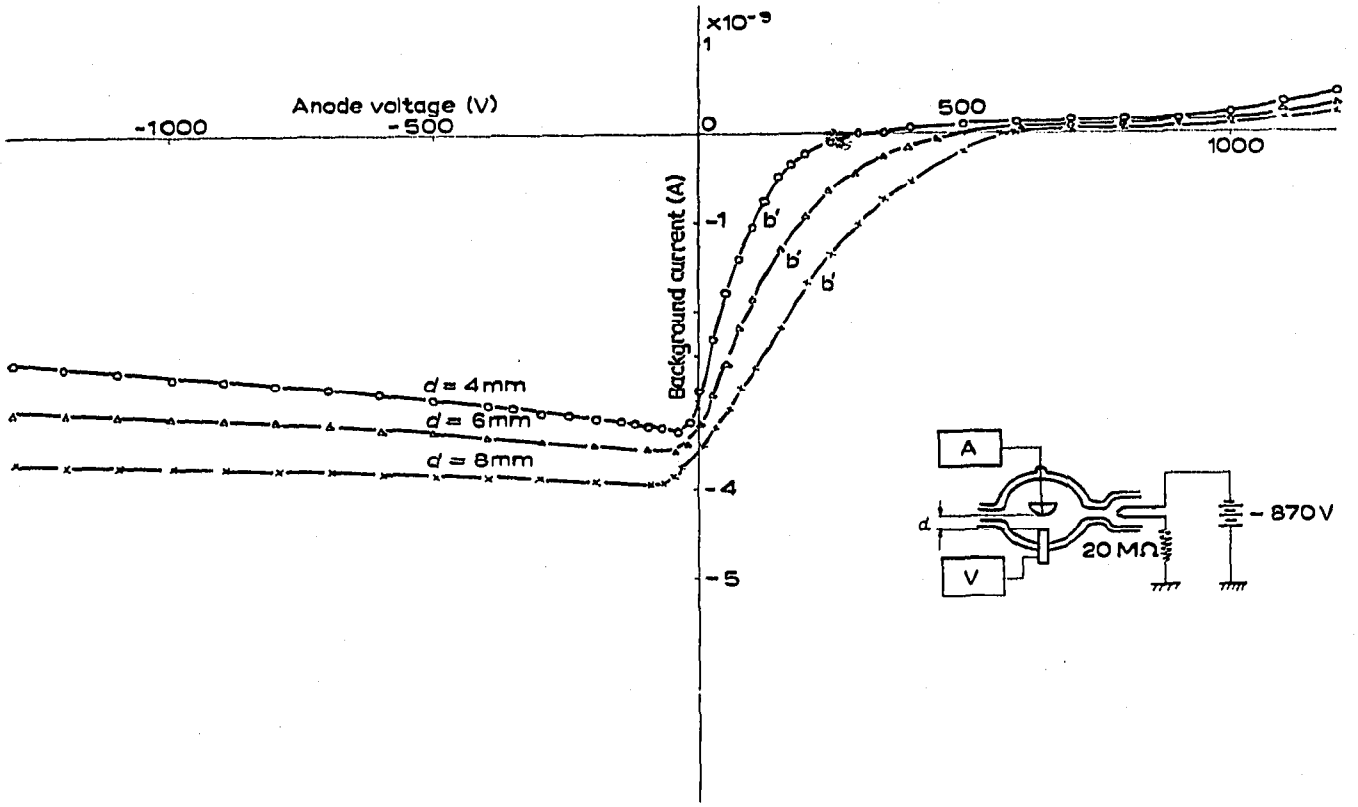

Fig. 9. Dependence of the background current upon the anode position. Helium flow = 20 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

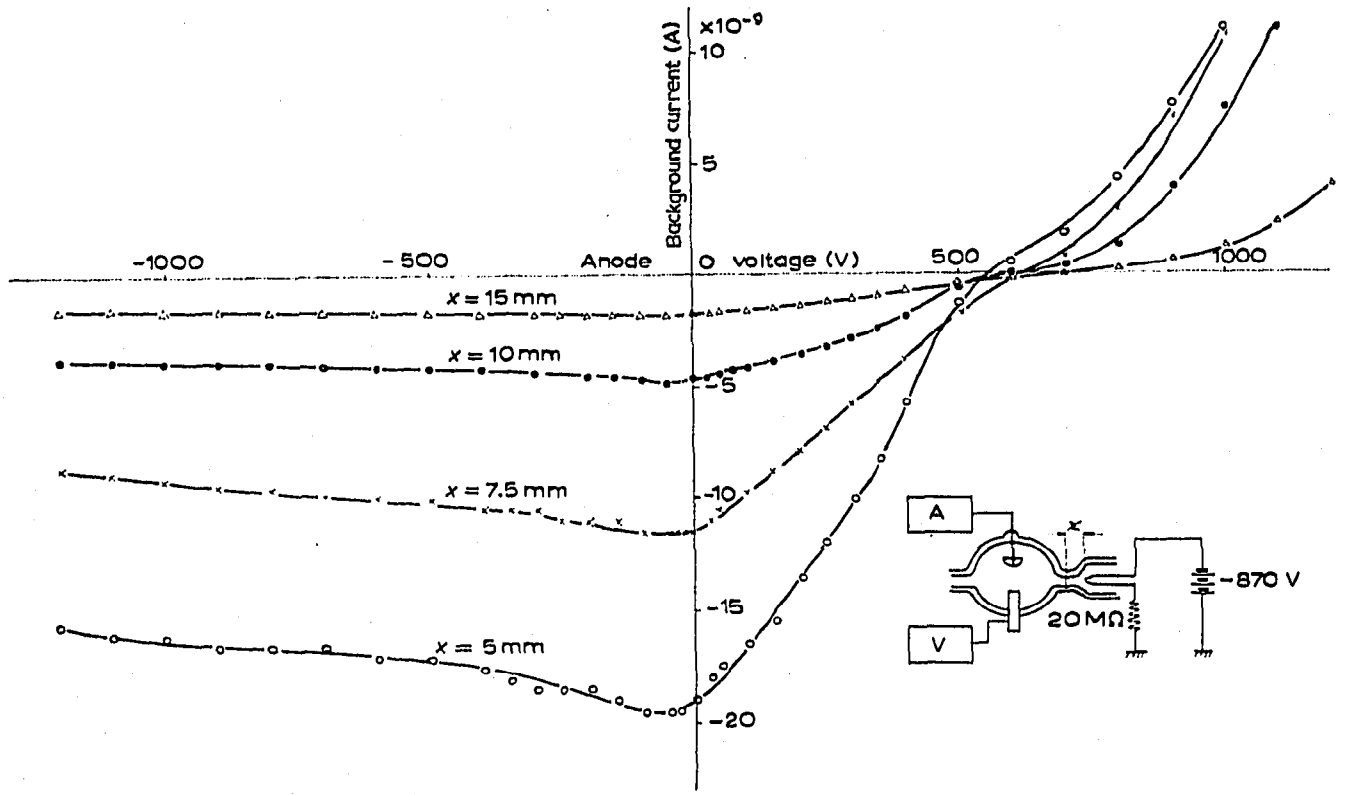

Fig. 10. Dependence of the background current upon the position of the discharge electrodes relative to the sensing chamber. Helium flow = 60 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

(*d*) *Effect of the flow rate of the discharge gas.* Fig. 11 shows the background current as a function of the helium flow at different anode voltages. It can be seen that the background current increases continually as the flow rate increases. This result seems to indicate that charged particles are entrained by the discharge gas into the sensing chamber, and it was on the basis of this observation that we postulated the "entrainment" theory in the previous paper.

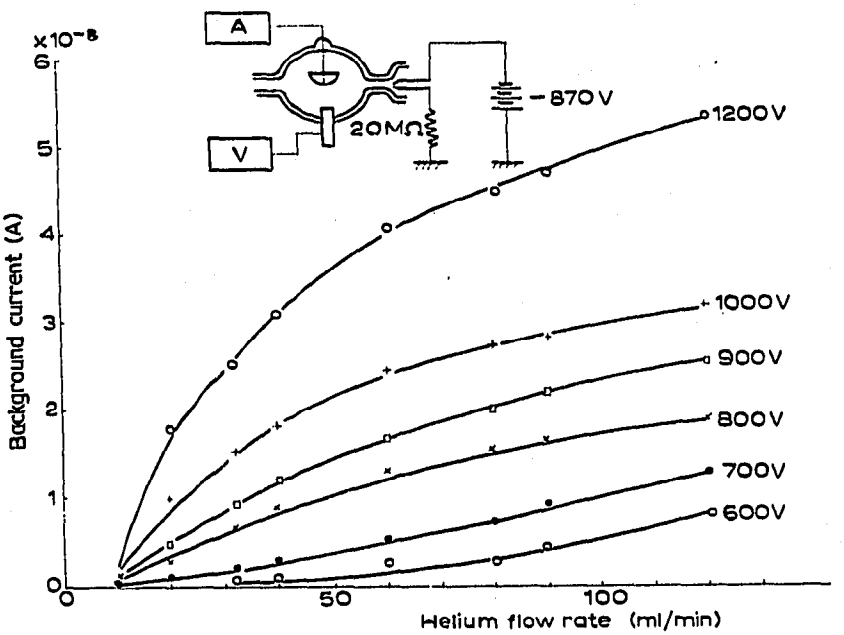

Fig. 11. Background current as a function of the helium flow at different anode voltages. Argon flow = 60 ml/min; discharge current = 30 μA.

Very recently the problem has been studied by NOREM[4] of the Perkin-Elmer Corporation with the same discharge detector. He measured the background current as a function of the helium flow in both the normal and the reverse direction, with no argon flow, and found that even in the case of the reverse flow, the current increased with the helium flow in the same way as in the normal-flow case. This disproves clearly the "entrainment" theory.

It might be expected, however, that at higher flow rates charged particles would have a much greater chance of separating from the discharge due to a turbulent action of the helium flow. These escaping charged particles, while negligibly small in number compared with those existing in the discharge path, would be of importance in determining the intensity of the background current.

Response for propane

The response of the detector varies to a great extent with the mode of its operation, *i.e.*, with the discharge circuit, the discharge current, the operating voltage and the flow rates of the carrier and the discharge gas. Measurements were made to investigate the effect of these factors on the response for propane.

(*a*) *Effect of the discharge circuit.* It has been shown that it is possible to increase the primary electron current by making the discharge potential highly negative with respect to the sensing chamber. This should result in more efficient ionization of the

sample and thus increase the sensitivity of the detector. As a test of this premise, the peak current of 0.0022 ml propane (gas volume) was measured, making simple alterations to the discharge circuit, while keeping other operational conditions unchanged.

The results of these measurements are summarized in Tables I and II. These tables are of interest in that they show the relative merit of the various discharge circuits. It can be seen that, for the case of the positive discharge (Table I), the background current is appreciably larger than the peak current, and that the higher the discharge potential, the larger the background current and the smaller the response. Thus, the positive discharge cannot be used advantageously in most circumstances. On the other hand, the negative discharge gives a peak current much larger than the background current (Table II). Furthermore, it is noted that the response increases as the discharge potential becomes more negative.

(b) *Effect of the helium flow.* According to Fig. 11, the number of electrons entering into the sensing chamber varies with the helium flow. This, together with the change of the gas composition in the sensing chamber, would affect the response of the detector.

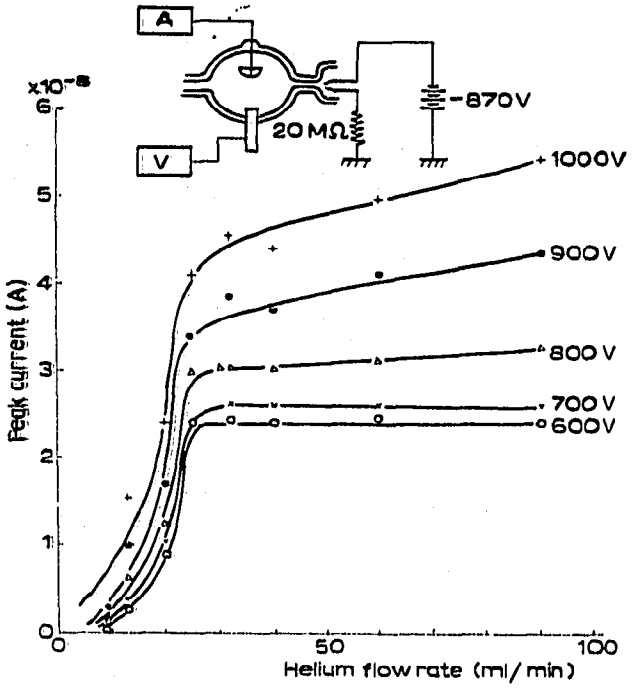

Fig. 12. Peak current as a function of the helium flow at different anode voltages. Sample = $4.5 \cdot 10^{-7}$ g/sec of propane; argon flow = 60 ml/min; discharge current = 30 μA.

To clarify this effect, measurements were made for a negative discharge of 30 μA at different anode voltages. The result obtained is given in Fig. 12. It can be seen that for the helium flow below 30 ml/min, there is a steep rise in the response, while above 30 ml/min this ceases to depend on the helium flow. The initial increase is attributable solely to the increase in the primary electrons, since, according to LOVELOCK[5], the change of the gas composition in the region of lower helium flow (the region of lower proportion of helium in argon) has no appreciable effect on the ionization efficiency. At helium flow higher than 30 ml/min, where the primary

TABLE I

EFFECT OF THE DISCHARGE CIRCUIT ON THE RESPONSE FOR PROPANE

(Discharge is excited by a positive high voltage supply)

Sample: propane 0.0022 ml. Temperature: 20°. Column: squalane 5 m. Carrier gas: argon, 60 ml/min. Discharge gas: helium, 60 ml/min. Discharge current: 30 μA.

Discharge circuit **	*Anode voltage* V	*Background current* A × 10^{9}	*Peak current*** A × 10^{9}
1	600	3.1	1.1
	700	2.9	2.3
2	600	9.0	1.2
	700	8.8	1.9
3	600	16.5	0.9
	700	16.0	1.3

* 1. A current limiting resistor of 20 MΩ is inserted between the high voltage supply and one electrode. The other electrode is at the earth potential. The discharge potential is positive and low.
2. A 10 MΩ resistor is inserted between the high voltage supply and one electrode. Also between the other electrode and the earth is inserted a resistor of 10 MΩ. The discharge potential is positive and medium.
3. One electrode is connected directly to the high voltage supply. Between the other electrode and the earth is inserted a 20 MΩ resistor. The discharge potential is positive and high.

** Peak current is the net deflection above the background current.

TABLE II

EFFECT OF THE DISCHARGE CIRCUIT ON THE RESPONSE FOR PROPANE

(Discharge is excited by a negative high voltage supply)

Sample: propane 0.0022 ml. Temperature: 20°. Column: squalane 5 m. Carrier gas: argon, 60 ml/min. Discharge gas: helium, 60 ml/min. Discharge current: 30 μA.

Discharge circuit *	*Anode voltage* V	*Background current* A × 10^{9}	*Peak current*** A × 10^{9}
1	600	0.74	13.0
	700	1.20	14.5
2	600	1.55	17.5
	700	2.2	19.0
3	600	2.8	23.0
	700	5.4	25.5

* 1. A current limiting resistor of 20 MΩ is inserted between the high voltage supply and one of the electrodes. The other is at the earth potential. The discharge potential is negative and low.
2. A 10 MΩ resistor is inserted between the high voltage supply and one of the electrodes. A resistor of 10 MΩ is also inserted between the other electrode and the earth. The discharge potential is negative and medium.
3. One of the electrodes is directly connected to the high voltage supply, and a 20 MΩ resistor is inserted between the other electrode and the earth. The discharge potential is negative and high.

** Peak current is the net deflection above the background current.

electron current still increases with the helium flow, increasing proportion of helium in argon starts impairing the ionization efficiency. These compensating effects give a flat region in the response-flow curves.

(*c*) *Linearity and limit of detection.* Fig. 13 shows the response of the detector as a function of the mass flow rate of propane at different anode voltages. As has been observed with the conventional argon ionization detector, a linear relationship was not obtained over the entire range of the mass flow.

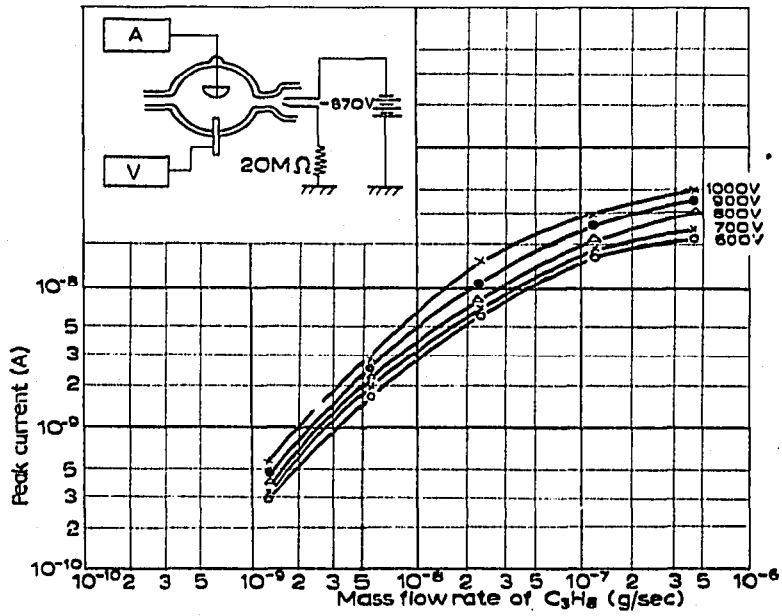

Fig. 13. The relationship between the peak current and the mass flow rate of propane at different anode voltages. Helium flow = 60 ml/min; argon flow = 60 ml/min; discharge current = 30 μA.

In order to obtain figures of the limit of detection, additional measurements were made, operating the detector at that anode voltage at which the cathode collects zero net background current. This condition allows us to make an accurate determination of the noise level of the detector. The results obtained are given in Table III. The table is arranged as follows: In the first column is given the helium flow rate, at

TABLE III

THE PERFORMANCE CHARACTERISTICS OF THE DETECTOR UNDER THE CONDITION OF ZERO NET BACKGROUND CURRENT

Sample: propane 0.0022 ml (mass flow rate: $4.5 \cdot 10^{-7}$ g/sec). Column: squalane 5 m. Temperature: 20°. Carrier gas: argon 60 ml/min. Discharge gas: helium. Discharge current: 30 μA.

Flow rate ml/min	*Background current (V = o) A*	*Anode voltage (i_0 = o) V*	*Noise current A*	*Peak current A*	Q_{min} *g/sec*	C_{min} *g/ml*
5	$-3.3 \cdot 10^{-10}$	580	$3 \cdot 10^{-13}$	$4.0 \cdot 10^{-10}$	$6.75 \cdot 10^{-10}$	$6.75 \cdot 10^{-10}$
10	$-1.25 \cdot 10^{-9}$	575	$1.1 \cdot 10^{-12}$	$1.5 \cdot 10^{-9}$	$6.6 \cdot 10^{-10}$	$6.6 \cdot 10^{-10}$
20	$-9.0 \cdot 10^{-9}$	570	$6.0 \cdot 10^{-12}$	$8.5 \cdot 10^{-9}$	$6.4 \cdot 10^{-10}$	$6.4 \cdot 10^{-10}$
30	$-1.7 \cdot 10^{-8}$	560	$1.6 \cdot 10^{-11}$	$2.1 \cdot 10^{-8}$	$6.8 \cdot 10^{-10}$	$6.8 \cdot 10^{-10}$
40	$-2.8 \cdot 10^{-8}$	550	$4.5 \cdot 10^{-11}$	$2.1 \cdot 10^{-8}$	$2.0 \cdot 10^{-9}$	$2.0 \cdot 10^{-9}$
60	$-5.1 \cdot 10^{-8}$	535	$2.0 \cdot 10^{-10}$	$2.05 \cdot 10^{-8}$	$8.8 \cdot 10^{-9}$	$8.8 \cdot 10^{-9}$

which measurement was made, and in the second column the background current at zero anode voltage. This quantity represents a measure of the primary electrons drawn to the sensing chamber. The third column gives the operating anode voltage at which the background current disappears. The fourth column gives the noise current at the operating voltage. In the fifth is given the peak current obtained on 0.0022 ml propane at a mass flow rate of $4.5 \cdot 10^{-7}$ g/sec. Columns six and seven give values of the minimum detectable quantity, Q_{min}, and of the minimum detectable concentration, C_{min}, which are calculated from the relations given by CONDON *et al.*[6].

From these data, it must be recognized that the experimental values of the limit of detection depend critically upon the flow rate of helium. At lower helium flow, $Q_{min} \approx 6.5 \cdot 10^{-10}$ g/sec and $C_{min} \approx 6.5 \cdot 10^{-10}$ g/ml, while at flow rates above 30 ml/min, Q_{min} and C_{min} increase with the flow rate.

It is difficult to say how much significance should be attached to the values of this table, because the noise current should depend on the conditions of measurement, *i.e.* on the stability of the high voltage supply for the discharge, the stability of the anode voltage, the uniformity of the helium flow and the bandwidth of the electrometer. Furthermore, the operating conditions of these measurements do not represent those giving the best values for Q_{min} and C_{min}, since at higher anode voltages the multiplication effects would improve the S/N ratio up to some optimum point, as in the LOVELOCK's detector.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. T. SEKI and Mr. S. TAKEI for their encouraging support and guidance during the course of this investigation, and to Mr. M. YAMAMOTO for his valuable discussions on various matters associated with this paper. He is also indebted for numerous stimulating suggestions to Mr. V. J. COATES of the Perkin-Elmer Corporation. Thanks are also due to Mr. S. D. NOREM for his helpful and stimulating discussions, and his kindness in reading the original manuscript. Mr. I. ASAKAWA has given the author his generous help throughout the experiments.

SUMMARY

A subsidiary discharge argon ionization detector, which uses helium as the discharge gas and argon as the carrier gas, is described. The properties of the discharge in the helium flow were first studied from the point of view of its suitability as a source of primary electrons. Next, the generation mechanism of primary electrons was investigated by measurements of the background current to the cathode. The background current measured as a function of the anode voltage was found to depend on the discharge potential with respect to the potential of the sensing chamber, which indicates that the transfer of charged particles from the discharge to the sensing chamber is due to an electrical force acting between the two chambers. From these results, a new technique of operation was developed. Finally the response was tested for propane, and the relationships between the response and the background current were discussed.

REFERENCES

[1] M. YAMANE, *J. Chromatog.*, 9 (1962) 162.
[2] J. E. LOVELOCK, *J. Chromatog.*, 1 (1958) 35.
[3] J. M. MEEK AND J. D. CRAGGS, *Electrical Breakdown of Gases*, Oxford University Press, 1953, p. 89.
[4] S. D. NOREM, personal communication.
[5] J. E. LOVELOCK, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 24.
[6] R. D. CONDON, P. R. SHOLLY AND W. AVERILL, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 35.