

## A NEW ARGON IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

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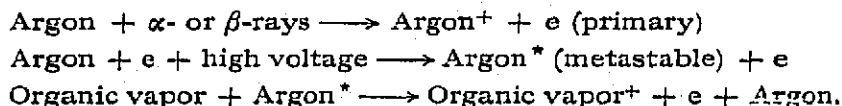
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(Received December 27th, 1961)

### INTRODUCTION

During recent years continuing efforts have been directed towards the development of various types of ionization detectors for gas chromatography. Two of these, namely the argon  $\beta$ -ray and the flame ionization detector, are extensively used because of their extremely high sensitivity to the component gases.

The argon  $\beta$ -ray ionization detector, which was developed by LOVELOCK in 1958<sup>1</sup>, is based on the principle that organic molecules are ionized by collision with metastable argon atoms. It has been shown that the reactions taking place within the ionization chamber may be represented as follows:



The emergence of an organic vapor from the chromatographic column can be detected and measured by an increase in the ionization current. In the reactions shown above the role of the radioactive source is principally to provide primary free electrons for securing the stability of the detector.

There are, however, several possible methods of producing primary free electrons, instead of using a radioactive source. For instance, LOVELOCK<sup>2</sup> suggested the possibility of utilizing a subsidiary discharge, such as corona discharge, silent low pressure discharge or radio-frequency discharge. Along these lines he proceeded to devise successfully a spark gap detector, with which he measured the breakdown potential as a function of the vapor concentration. But good stability of the ionization current could not be achieved.

More recently LOVELOCK<sup>3</sup> devised another type of detector, the photo-ionization detector. The details of its performance, however, have not yet been reported.

This paper is concerned with a new argon ionization detector. Its features are the following:

1. Primary electrons are generated by a self-sustained subsidiary discharge.
2. The subsidiary discharge is excited in the scavenging gas stream, ahead of the sensing chamber. A small fraction of electrons generated by this discharge passes into the sensing chamber with the scavenging gas.
3. The field-intensified ionization current is measured in the sensing chamber.

*General design*

## EXPERIMENTAL ARRANGEMENT

It is well known that the ionization properties of a corona discharge are very sensitive to impurities. However, as LOVELOCK<sup>2</sup> has shown, the use of a corona discharge by itself for the detection of impurities has the disadvantage that it is difficult to obtain a reliable and reproducible operation, inasmuch as the emission of electrons from the corona electrode is disturbed by the presence of impurities. Alternatively, it may be possible to utilize a corona discharge subsidiarily for generating free electrons and directing a fraction of them into an ionization chamber, where the field-intensified ionization current is to be measured. However, even when using a corona discharge as such, instability could not be avoided as long as the corona discharge was maintained in the atmosphere of the effluent gas. In this case, the signal current of the sensing electrode depends on the number of primary electrons, that suffers fluctuation as mentioned above.

With this fact in mind, we have attempted to design a suitable instrument and this is shown schematically in Fig. 1. With argon as carrier gas, it has two flow paths in parallel: (1) through a gas regulating valve, the sample-introducing device, column and detector (carrier gas flow), and (2) through a gas regulating valve, subsidiary discharge electrodes and detector (scavenging gas flow). The main feature of this system is the incorporation of the electrodes for the subsidiary discharge in the scavenging gas stream in front of the sensing chamber of the detector. This makes it possible to keep the subsidiary electrodes separated from the effluent gas and thus set up a stable discharge. A fraction of electrons generated by this discharge falls

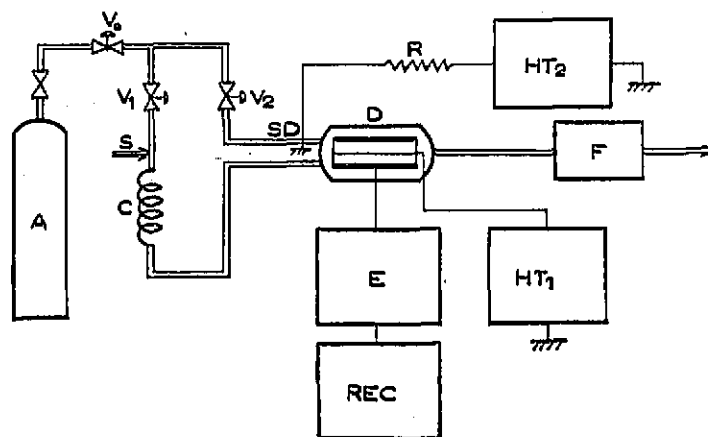


Fig. 1. Schematic diagram of apparatus. A = Argon cylinder;  $V_0$ ,  $V_1$ ,  $V_2$  = Gas regulating valves; S = Sample introducing device; C = Column; SD = Subsidiary discharge electrodes; D = Detector; F = Flow meter;  $HT_1$  = High voltage supply for detector; E = Electrometer; REC = Recorder;  $HT_2$  = High voltage supply for subsidiary discharge; R = Current limiting resistance.

into the sensing chamber with the flow of scavenging gas. The confluence of the carrier and the scavenging gas within the sensing chamber yields an ionization current with a steady level, and hence an increase in ionization occurs when an organic vapor emerging from the chromatographic column enters the chamber.

*The detector*

The detector used in this preliminary experiment is shown in Fig. 2 and the details

of its construction are given in Fig. 3. For easy construction, the detector housing is made of Kovar glass tube with an outer diameter of 30 mm and a length of 65 mm. The cathode, which also acts as an ion-collector, is a stainless steel cylinder of 20 mm outer diameter and 40 mm length. The anode, which is mounted along the axis of the cylinder, is made of 0.2 mm diameter tungsten wire.

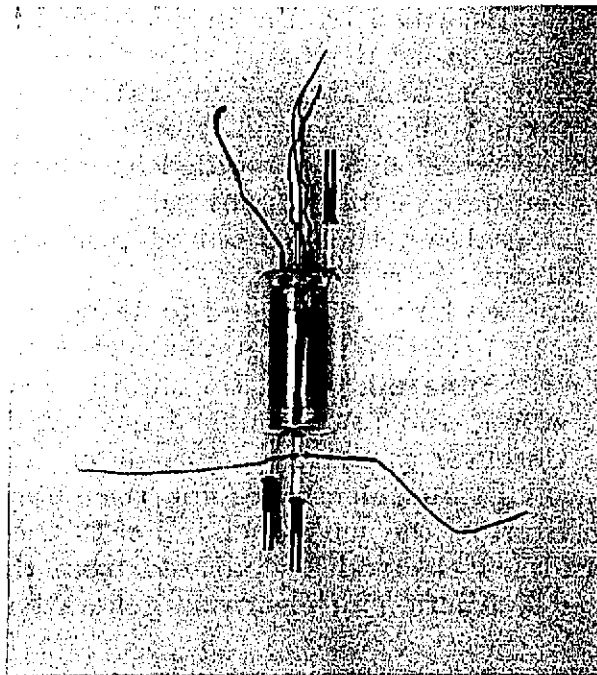


Fig. 2. Photograph of the detector.

The inlet and outlet tubes are sealed to each end of the envelope. They are made of Kovar glass tube, 5 mm o.d., and can be connected to the gas flow system by means of Kovar-to-glass joints.

The electrodes of the subsidiary discharge are incorporated in the tube for the scavenging gas inlet, located at a distance of about 10 mm from the envelope. The electrode construction found to be most convenient consists of two wires inserted opposite each other perpendicular to the gas flow; one of them is a tungsten wire 0.1 mm in diameter and the other a Kovar wire 0.5 mm in diameter.

In order to obtain a stable subsidiary discharge it is important to clean the surface of the electrodes thoroughly. Furthermore, it was found in our experiments that the stability depends critically upon the space between the electrodes, and that

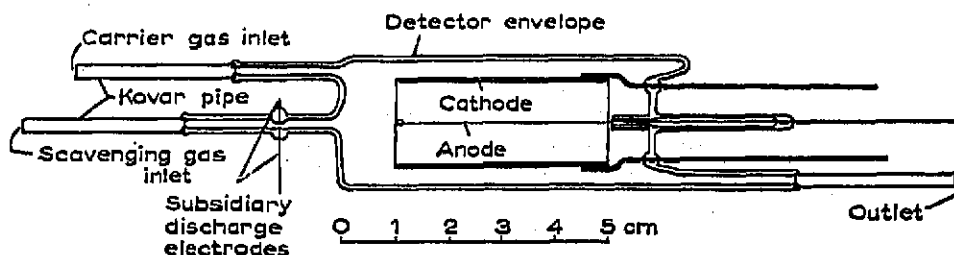


Fig. 3. Cross section of the detector.

fluctuation is more likely to occur with somewhat larger spaces. Therefore it is necessary to mount the electrodes close to each other (*ca.* 0.1 mm). This is probably because a short gap discharge is in essence not very different from low pressure discharge, and thus a stable discharge may be maintained easily at relatively low applied potentials.

## RESULTS

### *Subsidiary discharge*

Experiments were first carried out on the characteristics of the subsidiary discharge in order to prove that it is stable enough to serve as a source of primary electrons. Fig. 4 shows current-potential curves at a scavenging gas flow rate of 12 ml/min. The solid curves represent the ionization current as a function of the potential of the high voltage supply, measured with circuits of current-limiting resistance 100 M $\Omega$

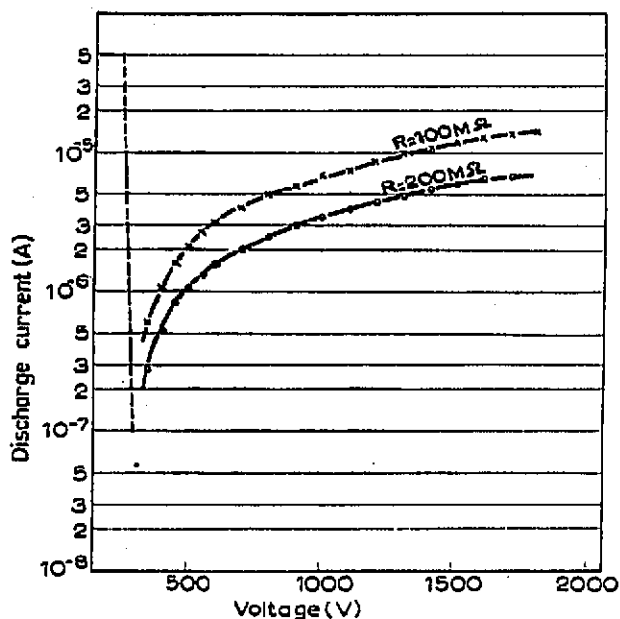


Fig. 4. Current-voltage curves for subsidiary discharge. Solid curves show the discharge current as a function of the potential of the high voltage supply, while the dashed curve shows the discharge current as a function of the inter-electrode potential.

and 200 M $\Omega$ , respectively. Until the potential reaches about 300 V, the starting potential of the discharge, there is no appreciable current (10<sup>-13</sup> A). At a potential slightly higher than 300 V, pulses of discharge start suddenly, accompanied by a faint emission of light. Thereafter, with increasing potentials, the frequency of the intermittent discharge rises very rapidly at first, while later it gradually goes over to a continuous and steady discharge with a current of several micro-amperes.

The variation of the current as a function of the potential is shown more clearly in the current recordings given in Fig. 5, in which it can be seen that stable discharge is established at all potentials above 500 V. Thus in this region of potential the subsidiary discharge may be used as the source of primary electrons.

The manner in which this discharge was maintained is easily understood from the dashed curve in Fig. 4, which shows the relation between current and interelectrode

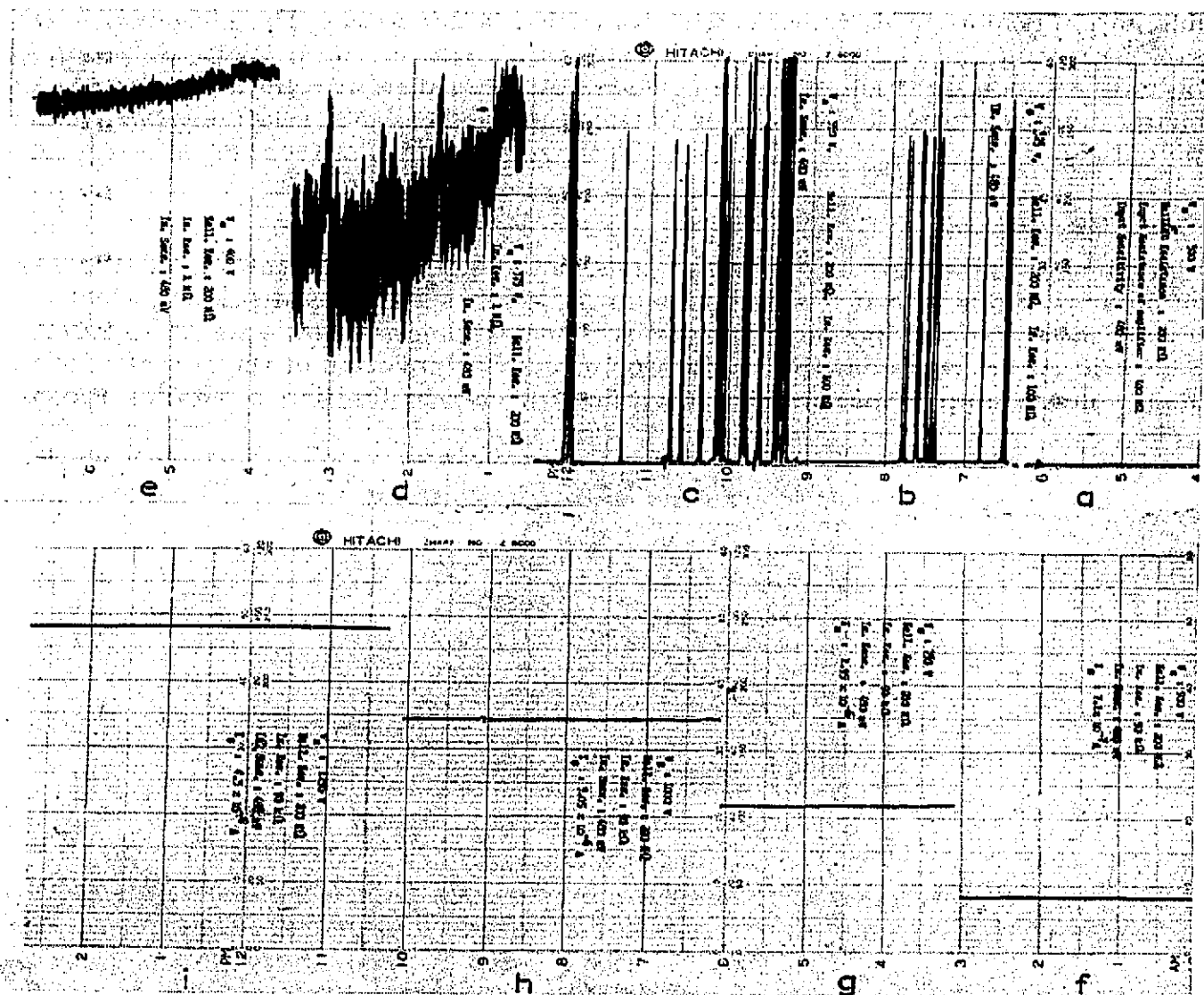


Fig. 5. Recorded curves for subsidiary discharge current. Note stable discharge being established for potentials above 500 V. (a)  $V = 300$  V; (b)  $V = 325$  V; (c)  $V = 350$  V; (d)  $V = 375$  V; (e)  $V = 400$  V; (f)  $V = 500$  V; (g)  $V = 750$  V; (h)  $V = 1000$  V; (i)  $V = 1250$  V.

potential. The vertical rise of the current at a critical voltage proves clearly that at that voltage the immediate breakdown into spark occurred, after which a glow discharge of a small current was maintained without the appearance of corona. Since the glow discharge is less affected by external disturbances and is thus more stable than the corona discharge, it is more suitable as a source of primary electrons. This immediate breakdown into spark occurs only when the gap is less than a certain critical value, called the corona point distance, as KIP<sup>4</sup> had found when investigating corona discharge.

Despite the results of the experiments presented here, it must be borne in mind that, as mentioned in the preceding section, the characteristics of the discharge depend critically upon the dimensions of the electrodes and the space between them. This disadvantage may be overcome by exciting the discharge in an atmosphere of

helium, in which it is more easily and more stably sustained than in argon<sup>6</sup>. A gas chromatographic method using argon as carrier gas and helium as scavenging gas, with a subsidiary discharge excited in the latter, is now under investigation.

#### *The background current*

In Fig. 6 the background current flowing between the detecting electrodes is shown. The curves were made at different values of the subsidiary discharge current, the gas flow rate being kept constant (carrier gas flow of 23 ml/min and scavenging gas flow of 12 ml/min).

It can be seen that the background current is about  $10^6$  times less than the subsidiary discharge current, which indicates that only a very small fraction of electrons, generated by the discharge, can survive long enough to reach the sensing chamber.

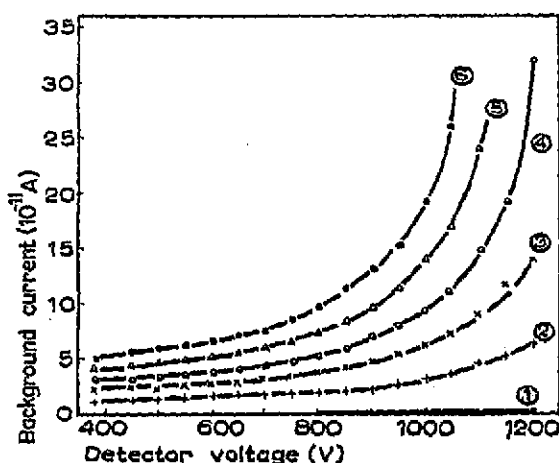


Fig. 6. Curves for background current plotted against detector voltage at various values of the subsidiary discharge current. Carrier gas flow 23 ml/min. Scavenging gas flow 12 ml/min. Subsidiary discharge current: (1) 0; (2)  $2 \cdot 10^{-6}$  A; (3)  $4 \cdot 10^{-6}$  A; (4)  $6 \cdot 10^{-6}$  A; (5)  $8 \cdot 10^{-6}$  A; (6)  $10 \cdot 10^{-6}$  A

The much smaller amount of background current than that of the conventional argon ionization detector has an advantage in that even with a high input resistor of the electrometer it can be easily suppressed to zero base line. Moreover, it should be noted that since the ionization efficiency depends on the intensity of the background current, the sensitivity can only be controlled by varying the current of the subsidiary discharge.

In Fig. 7 the background current plotted against the flow rate of the scavenging gas is shown. The linear relationship indicates clearly that primary electrons are not generated in the sensing chamber by photo-ionization, but are conveyed by the scavenging gas. Although the scavenging gas dilutes the concentration of the component gas it is to be expected that the increase in the background current with the gas flow will compensate the reduction of the ionization efficiency.

The stability of the background current depends, of course, mainly on the stability of the subsidiary discharge. It was found that preliminary ageing by running the discharge at a relatively large current is necessary to obtain a good base line stability. Under optimum operating conditions, the background noise can be reduced to about  $1 \cdot 10^{-13}$  A.

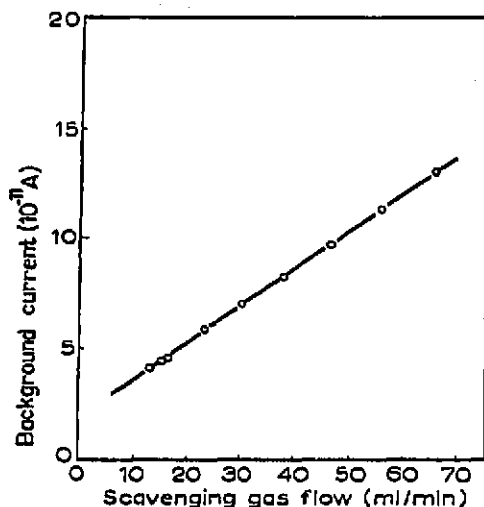


Fig. 7. Background current as a function of the flow rate of the scavenging gas. Detector voltage 600 V. Subsidiary discharge current  $6 \cdot 10^{-6}$  A. Note the linear increase in the background current with the flow of scavenging gas.

### Performance

In order to estimate the sensitivity of the detector, a three-way stopcock was employed to introduce small quantities of test gases. The stopcock shown in Fig. 8 was so designed that one of the paths is connected to a vacuum-gas filling system and, on turning the stopcock, the confined test gases are entrained by the carrier gas. In practice, the test gases were introduced as argon-sample gas mixtures at various concentrations and pressures.

In Fig 9 is shown the sensitivity, in terms of coulombs/g, to propane over a range from  $10^{-8}$  to  $10^{-6}$  g at various values of detector voltage and a subsidiary discharge current of  $5 \cdot 10^{-6}$  A. It can be seen that the sensitivity is nearly constant over a range up to about  $10^{-6}$  g of propane and that at large quantities it begins to fall. Phenomenologically, as the quantity of propane increases above  $10^{-6}$  g, the peak height tends to saturate gradually, and ultimately peak inversion occurs showing

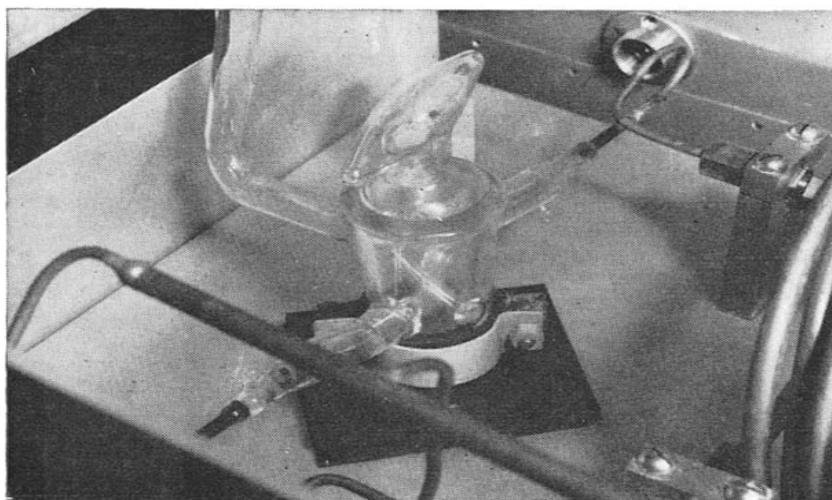


Fig. 8. Three-way stopcock for sample introduction.

double peaking. These quenching effects, as was observed by CONDON *et al.*<sup>6</sup>, seem to be characteristics of all types of argon ionization detectors.

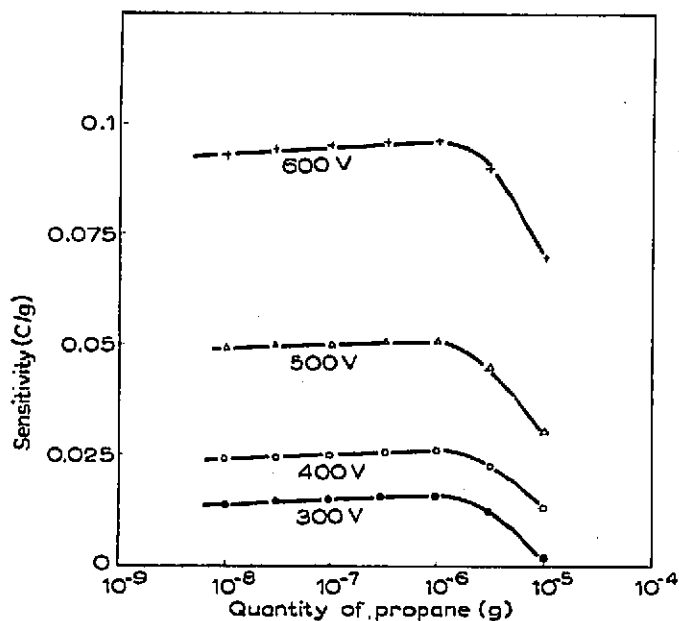


Fig. 9. Sensitivity to propane at various values of detector voltage indicated by the figures on the curves. The subsidiary discharge current is  $5 \cdot 10^{-6}$  A.

Fig. 10 shows the sensitivities to  $C_2$ - $C_5$  paraffin hydrocarbons as a function of detector voltage. Each curve was obtained with a quantity of  $5 \cdot 10^{-7}$  g at a subsidiary discharge current of  $5 \cdot 10^{-6}$  A. The results show a progressive increase in sensitivity with increasing length of the carbon chain. Furthermore it should be noted that there are appreciable differences in sensitivity between those gases for which the ionization potential lies below or above the metastable potential of argon.

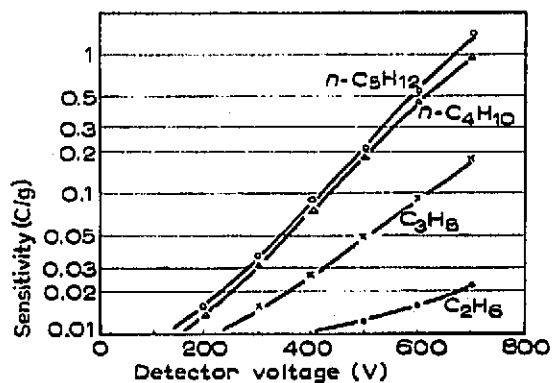


Fig. 10. Sensitivities to  $5 \cdot 10^{-7}$  g of ethane, propane, *n*-butane and *n*-pentane plotted against detector voltage. The subsidiary discharge current is  $5 \cdot 10^{-6}$  A.

As an example of analyses carried out with the ionization detector, three chromatograms are given in Fig. 11. They were obtained on 0.13 ml samples (gas volume) of



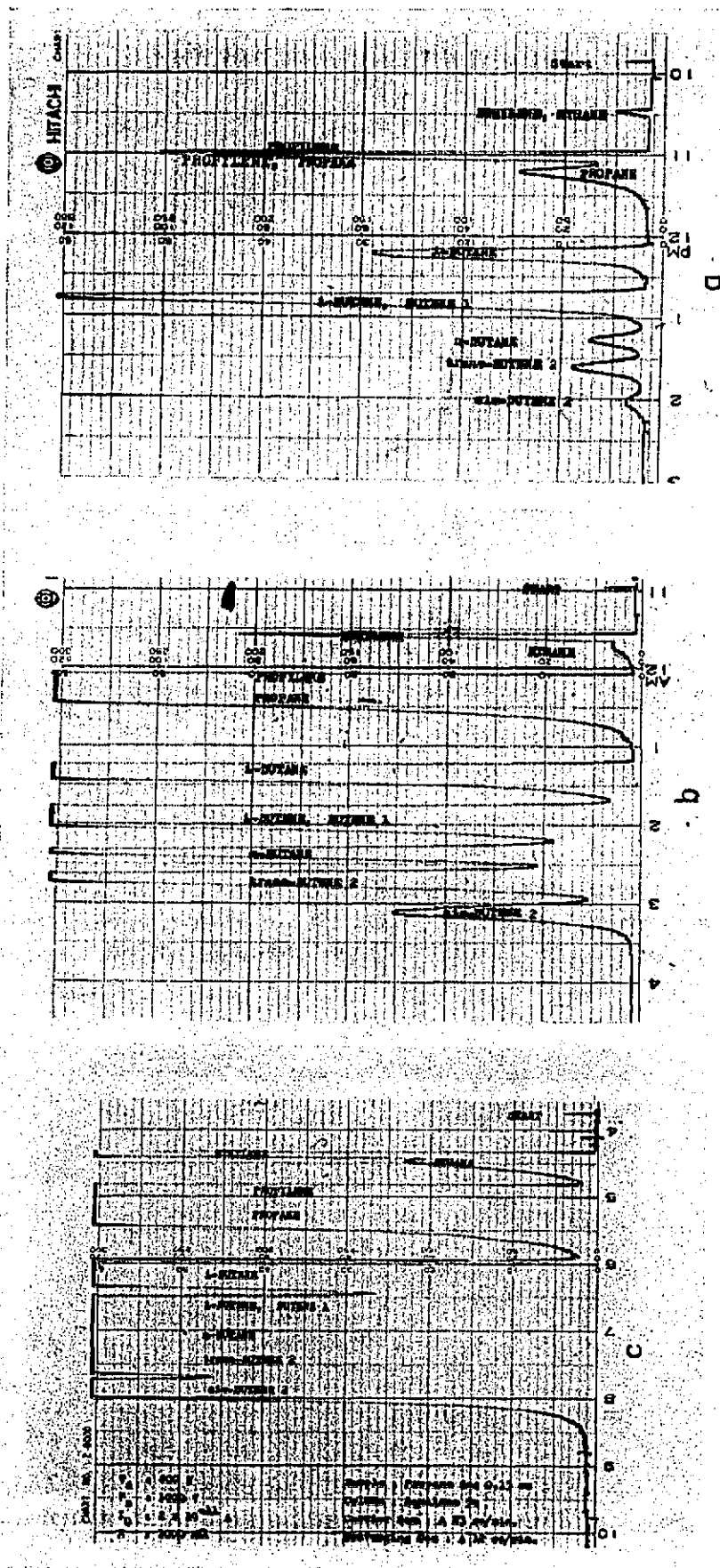


Fig. 11. Chromatograms of 0.13 ml C<sub>2</sub>-C<sub>4</sub> hydrocarbon mixtures. (a) Full scale: 5 · 10<sup>-9</sup> A. (b) Full scale: 5 · 10<sup>-10</sup> A. (c) Full scale: 5 · 10<sup>-11</sup> A.

C<sub>2</sub>-C<sub>4</sub> hydrocarbon mixtures under the following conditions:

Argon carrier gas	23 ml/min
Argon scavenging gas	12 ml/min
Column	Squalane 5 m
Temperature	20°
Subsidiary discharge current	4 · 10 <sup>-6</sup> A
Background current	2 · 10 <sup>-11</sup> A
Detector voltage	400 V
Input resistance of electrometer	1 · 10 <sup>9</sup> Ω.

The whole appearance of the chromatogram is shown in Fig. 11a. But it must be noted that when the sample contained 50.5% of propane (1.28 · 10<sup>-4</sup> g) and 22% of propane (5.35 · 10<sup>-5</sup> g), double peaking occurred. This is an example of overloading of the sample.

For the minimum quantity that can be detected by the detector, CONDON *et al.*<sup>6</sup> gave the following relation:

$$\text{Min. det. (g/sec)} = \frac{2 \times \text{noise (A)}}{\text{signal (A)/quantity (g)/band width (sec)}}$$

As can be seen in Fig. 11b, 6.5 · 10<sup>-7</sup> g *cis*-butene (0.2% of the sample) gives a peak of 2.1 · 10<sup>-10</sup> A with a band width of 70 sec, whereas in Fig. 11c it can be seen that the noise current is 1 · 10<sup>-12</sup> A or less. Thus the minimum amount of *cis*-butene that can be detected is 8.9 · 10<sup>-11</sup> g/sec. Though this value is slightly inferior to that of LOVELOCK's simple detector<sup>7</sup>, we may expect that a great improvement will be obtained with a micro version of our detector.

#### *Effect of the background current*

It was found that the detector operated stably even when the background current was reduced to 5 · 10<sup>-12</sup> A, the minimum value in our experiments, as long as a stable subsidiary discharge was maintained. But if the high voltage applied to the discharge electrode was reduced to zero, the operation was not satisfactory, because no primary electrons could exist in the chamber. Under these circumstances no peaks were observed at a detector voltage below 1000 V. If the voltage was increased further, peaks corresponding to easily ionizable components appeared sharply. As an example, a chromatogram obtained on the same sample is shown in Fig. 12.

The results of this analysis seem to contradict to those obtained by HAAHTI *et al.*<sup>8</sup> who reported that their detector operated successfully even without a radioactive source. It should, however, not be overlooked that in the absence of a radioactive source they observed an appreciable background current, though it is not clear where the primary electrons came from.

It is clear from what has been said above that the existence of primary electrons is essential. As regards the optimum intensity and the minimum safe operating intensity of the background current, not enough data are at hand at present to permit of discussion.

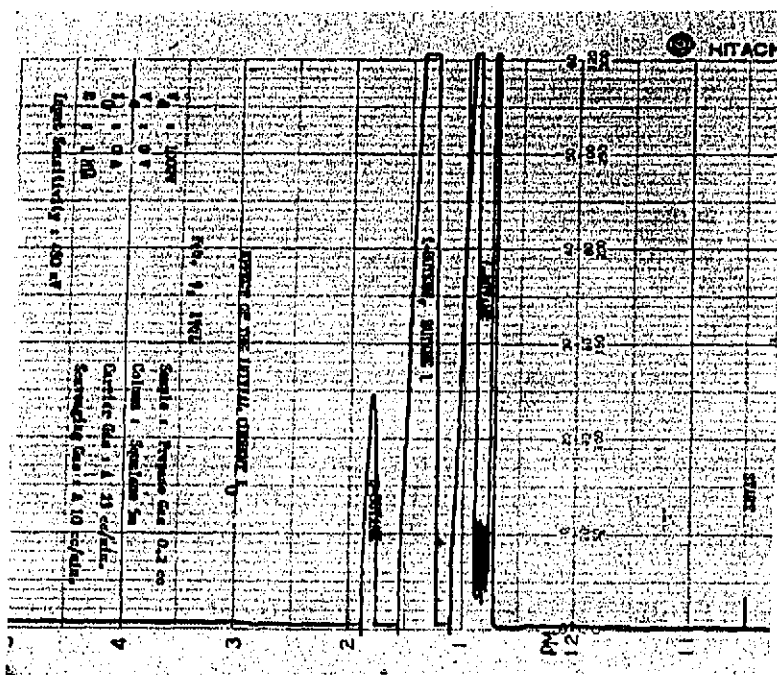


Fig. 12. Chromatogram of 0.2 ml  $C_2-C_4$  hydrocarbon mixtures. Background current is 0.

#### ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. M. SUGAWARA and Dr. S. TAKEI for their encouraging support and guidance throughout these experiments, and to Mr. M. YAMAMOTO for his valuable discussions and his examination of the manuscript.

#### SUMMARY

This paper is concerned with a new argon ionization detector. Its features are the following:

1. Primary electrons are generated by a self-sustained subsidiary discharge, instead of by means of a radioactive substance.
2. The subsidiary discharge is excited in the scavenging stream, ahead of the sensing chamber. A small fraction of electrons generated by this discharge passes into the sensing chamber with the flow of the scavenging gas.
3. Field-intensified ionization current is measured in the sensing chamber.

Details of the construction of the detector, the characteristics of the subsidiary discharge and performance of the detector are described.

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