A FLAME IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

A. E. THOMPSON

The Dyson Perrins Laboratory, Oxford (Great Britain)

This paper describes a modified form of the single jet flame ionization detector of McWILLIAM AND DEWAR[1]. The difference between the modified and the original form of the apparatus lies mainly in the electrical circuit of the amplifier. With the amplifying circuits described below the modified form of the detector has exhibited good base line stability and high sensitivity.

The realizable sensitivity of a detector for gas chromatography depends upon the acceptable signal to noise ratio as presented on the recorder chart, therefore the base line drift and noise level of detecting and measuring apparatus should be as low as possible. It is convenient to consider separately the two main parts of a flame ionization detector, the combustion chamber (detector) and electronic amplifier.

A reliable detector is simple to design and construct but a suitable amplifier is more of a problem, as it requires to have a very high input resistance, low output resistance, low noise level, and a high degree of linearity between input and output if peak areas are to be measured.

The amplifiers to be described have all these features, several have been constructed, the measured noise level of one is stated, and a gas chromatogram using this with a flame detector is shown.

THE DETECTOR

Details of the construction of the detector are shown in the scale drawing (Fig. 1) which is self-explanatory.

Normally hydrogen has been used as the carrier gas, but the apparatus is so constructed that nitrogen may be employed when necessary and mixed with hydrogen after its emergence from the column. The narrow bore of the three way tube between the column and the jet ensures that when nitrogen is used there is no diffusion of hydrogen into the column and no escape of eluted material through the tube supplying the hydrogen. The air which is supplied to the combustion chamber is filtered through glass wool, because, as McWILLIAM AND DEWAR have observed, even small particles of dust cause large disturbances.

It has been found that electrical insulation of a high order between the probe (gauze) and earth, and the use of stationary phases of very low volatility are essential for good base line stability. The first of these requirements is met by using insulators with a long tracking path over their surface and made of ceramic, which is a better

References p. 154.

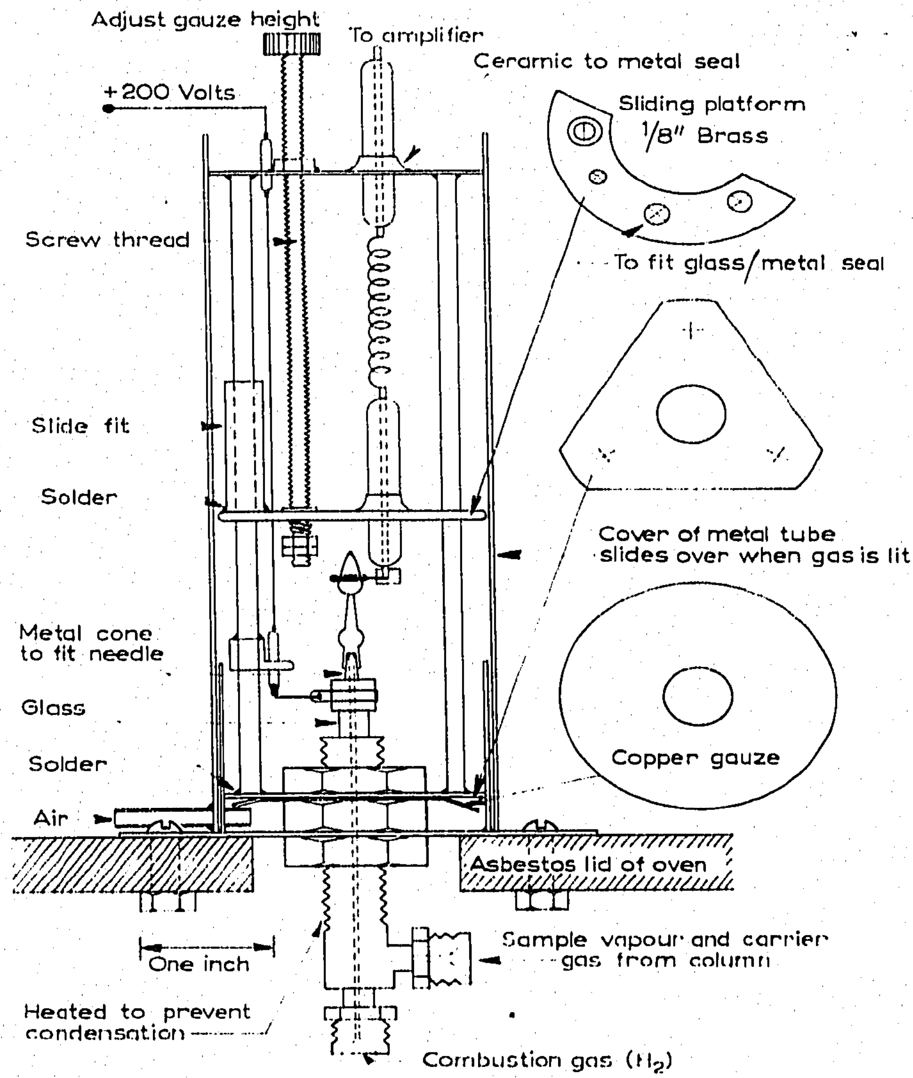

Fig. 1.

insulator than glass at high temperatures. Ocasionally it was noticed that the insulation deteriorated owing to the deposition of products of combustion on the ceramic-to-metal seals. To obviate this a metal screen (not shown in the diagram) was inserted between the flame and the seals.

AMPLIFIERS

It is necessary when designing an amplifier for this application to consider the requirements of the pen recorder which is to be used. Most laboratories using gas chromatography apparatus have potentiometric pen recorders intended for use with thermal conductivity cells. Such recorders have a sensitivity of one or two mV full scale deflection and therefore have a limitation regarding the value of electrical resistance which may be connected across their input terminals. Usually 500 Ω is the maximum which may be employed if the correct pen response time is to be obtained. It is of

References p. 154.

course desirable to keep the electrical circuits simple in the interests of reliability, but unfortunately it is not possible to design an amplifier using only one battery-type electrometer valve if it is to have a voltage gain of unity and an output resistance of 500 Ω. Since it is desirable to have high linearity between input and output voltage for an input of + and — 25 V, it is more convenient to use one of the multi-valve circuits to be described.

Alternative amplifying circuits are shown in Figs. 2 and 3. The first is a modification of a circuit described by SCROGGIE[2]. It is often assumed that an amplifier of this

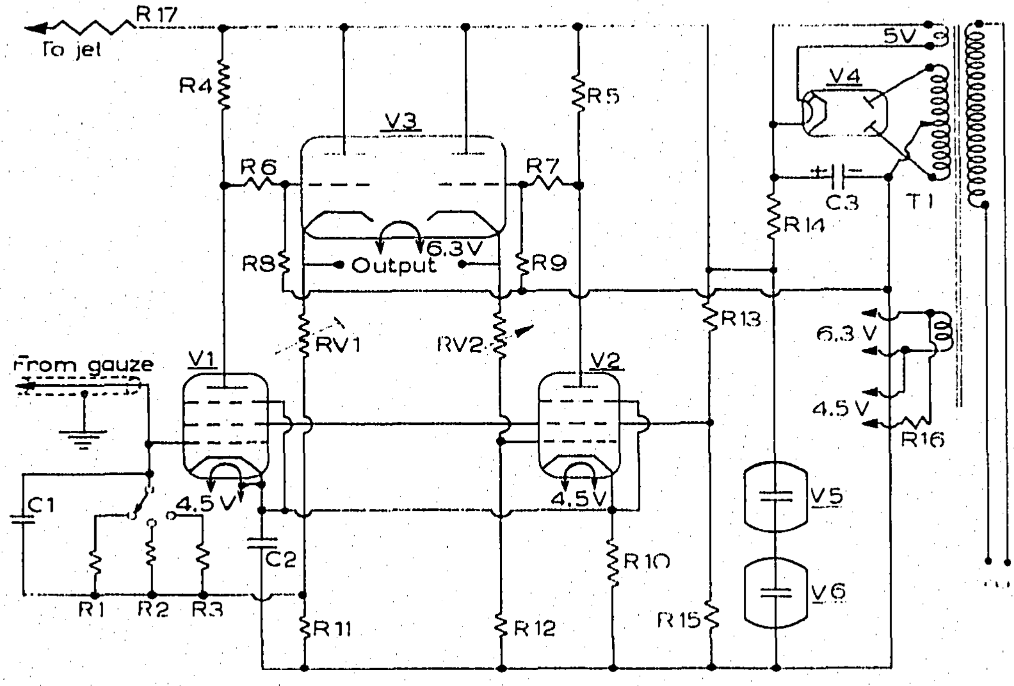

Fig. 2. Resistors: 1. $1 \cdot 10^9$ Ω; 2. $3 \cdot 10^9$ Ω; 3. $1 \cdot 10^{10}$ Ω; 4, 5. 820 kΩ, 2%, ½ W; 6, 7. 680 kΩ, 2%, ½ W; 8, 9. 2.2 MΩ, 5%, ½ W; 10. 470 kΩ, 5%, ½ W; 11, 12. 12 kΩ, 5%, 2 W; 13, 15. 82 kΩ, 5% 1 W; 14. 2.2 kΩ, 10%, 5 W; 16. 5.6 Ω, 10%, 2 W; 17. 1 MΩ, 20%, ½ W. RV_1: 500 Ω. Preset gain control. RV_2: 500 Ω. Variable zero control (panel mounting). Capacitors: C_1. Polystyrene, value as required (0.001 μF?); C_2. 0.1 μF, 150 V; C_3. 8 μF, 500 V. T_1 Mains transformer. Primary as required for local mains supply. Secondary: 350–350 V, 80 mA; 6.3 V, 2 A; 5.0 V, 2 A. Valves: V_1 and V_2. Type ME1400 (Mullard); V_3. Type ECC81 (Mullard) or 12AT7; V_4. Type 5Z4; V_5. Type VR/150/30; V_6. Type VR105/30. Input switch: One pole 3 way high insulation.

type is inherently stable, but it must be remembered that it is a high voltage gain amplifier with negative feedback, and phase shift within the amplifier may possibly cause oscillation of a high amplitude. If this happens it may well be that the amplifier is operating outside its correct characteristics, saturated, with V_1 control grid current flowing during part of each cycle of oscillation, exhibiting blocking and low input resistance. 50 c/sec will be introduced into the circuit if the 6.3 heater voltage is not at a definite fixed potential, and it should be connected to a valve cathode (V_1) as shown. As a precaution against A.C. pickup on the input circuits, and amplifier instability, the capacitor C_2 will short out alternating voltage, whatever its source. The zero stability of this type of amplifier also requires that the heaters of V_1, V_2 and V_3 be "aged" by running them for several hundred hours.

References p. 154.

A potentiometric pen recorder is connected to the output terminals of the amplifier through a suitable voltage attenuator. A 1 mA moving coil recorder can be used equally well with this type of amplifier.

Since the recorders which were available for use with the amplifier would not tolerate more than a few per cent of their input signal to consist of alternating voltage of supply frequency, A.C. pickup on the input of the amplifier must be filtered out. The amplifier was connected to the collector probe by a few metres of 75 Ω coaxial cable of approximately 100 μμF capacity per metre, which together with the input

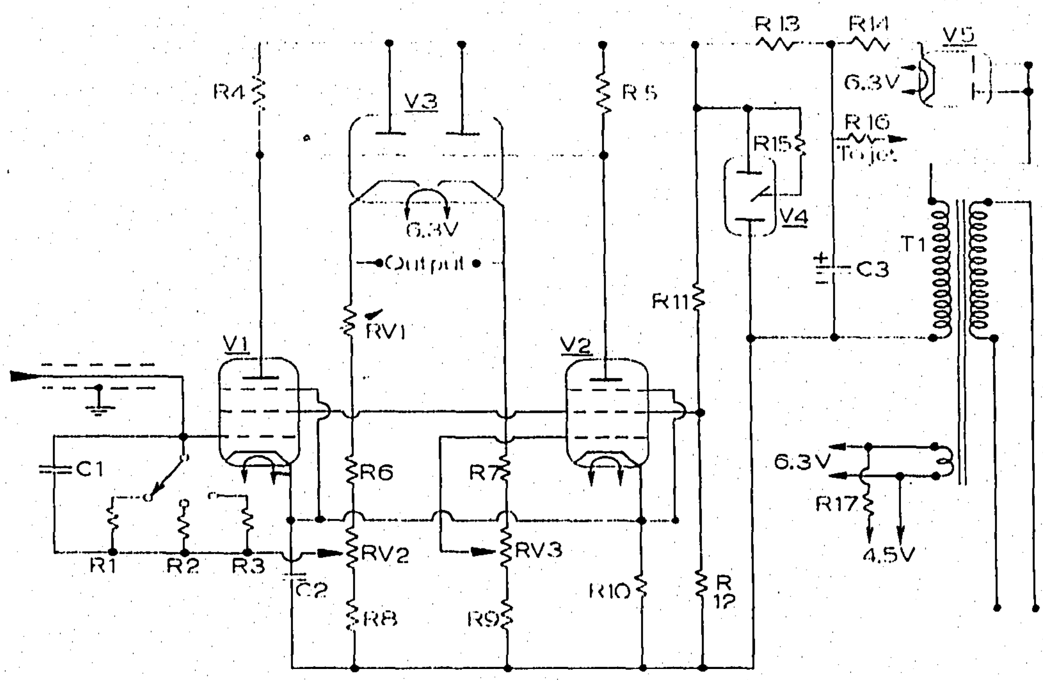

Fig. 3. Resistors: 1. $1 \cdot 10^9\ \Omega$; 2. $3 \cdot 10^9\ \Omega$; 3. $1 \cdot 10^{10}\ \Omega$; 4, 5. 470 kΩ, ½ W, 2%; 6, 7. 33 kΩ, 5%, 1 W; 8, 9. 10 kΩ, 5%, 1 W; 10. 100 kΩ, 5%, ½ W; 11. 150 kΩ, 5%, ½ W; 12. 750 kΩ, 5%, ½ W; 13. 10 kΩ, 20%, 2 W; 14. 220 Ω, 20%, ½ W; 15, 16. 1 MΩ, 20%, ½ W; 17. 5.6 Ω, 10%, 2 W. RV_1: 2 kΩ. Variable zero control (panel mounting). RV_2: 1 kΩ. Preset zero control. RV_3: 1 kΩ Preset gain control. Capacitors: C_1. Polystyrene, value as required; C_2. 0.1 μF, 150 V; C_3. 16 μF. 500 V. T_1 Mains transformer. Primary as required. Secondary: 250 V, 30 mA; 6.3 V, 2 A. Valves: V_1 and V_2. ME1400 (Mullard); V_3. ECC81 (Mullard); V_4. 150B3 (Mullard); V_5 EZ80 (Mullard) or 6 X 4 or 6 X 5.

resistor used had a time constant of 1 or 2 seconds, sufficient to attenuate the A.C. pickup without appreciably increasing the response time of the pen recorder. Further capacitance can be made available, if necessary, by the use of polystyrene capacitors connected in parallel with the high value input resistors. These capacitors are shown as C_1 in the amplifier circuits.

Each amplifier is housed in a metal box of about 8 l capacity, large enough to keep the stray magnetic field of the mains transformer away from the valves, which may be separately screened. If the transformer is rated at much higher output currents than the circuit requires, so that its core operates well away from magnetic saturation, and is supplied in a metal shroud or box, it will not cause trouble. The coaxial cable from the detector is taken to the amplifier through its front panel without plug or

References p. 154.

socket and direct to the control grid of the pentode valve V_1. The moving contact of a good quality ceramic switch is also taken directly to the grid. It is important that these input components should be kept clean and dry. The resistors are held with thermal shunts during soldering, their body being untouched, and they are mounted away from the other components in the interests of temperature stability. If a slow drift of the base line is observed it may be due to the fact that insufficient time has been allowed for all components in the amplifier to reach their final temperature, and half an hour or so should be allowed for this. Other possible causes are the use of low grade or overrun components, and the mounting of temperature sensitive resistors, such as the pentode anode load resistors R_4 and R_5 too close to warm components. If identical resistors are mounted close together the effects of their resistance change due to heating tend to be cancelled out by the circuit. The pentodes should be mounted close together and away from the other valves. All valve holders should be of good quality as leakage across pins could produce noise on the base line.

Base line instability due to circulating earth currents may be avoided by earthing

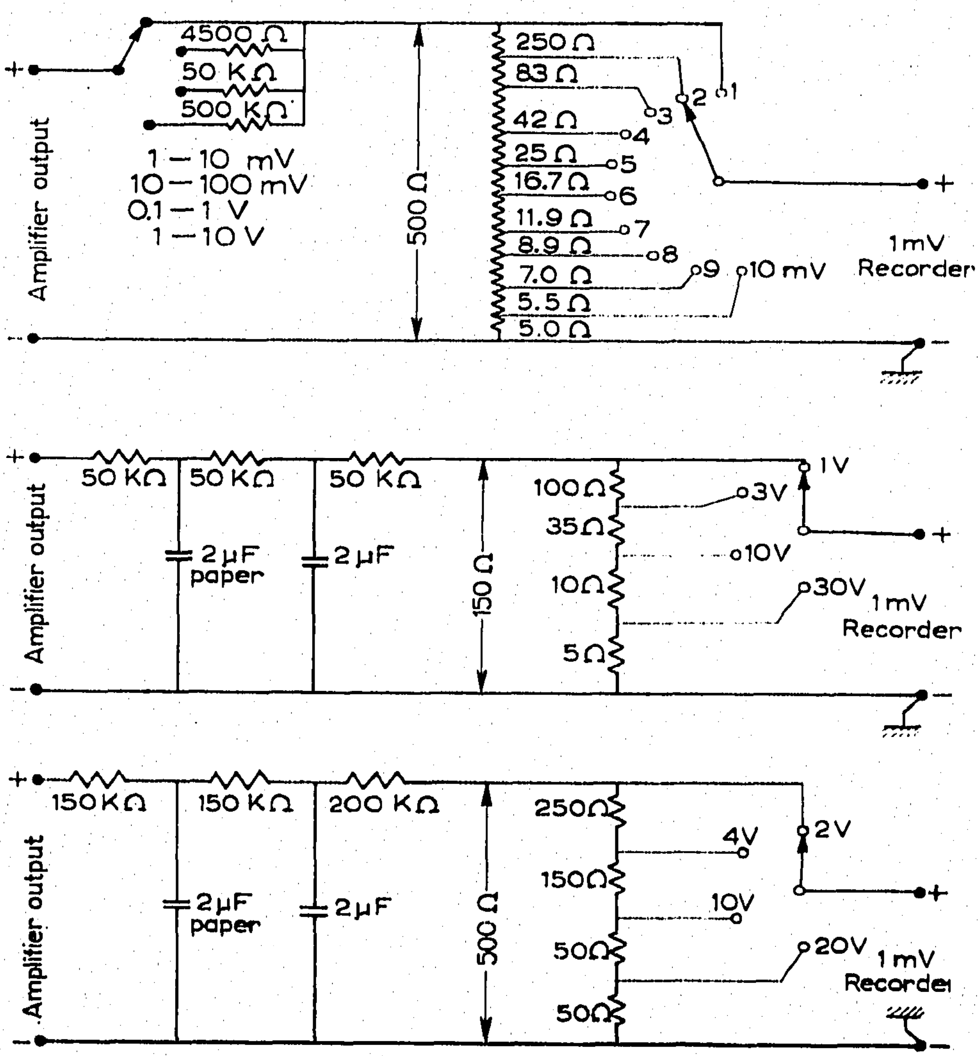

Fig. 4.

References p. 154.

the whole apparatus at one point, the negative input terminal of the pen recorder. The ceramic switch, high value resistors and pentode valves should be screened from dust, moisture, light and other radiation.

When the measurement of peak areas is required an Electo Methods integrator motor counter can be connected directly to the output terminals of the amplifier, which is particularly suitable for the purpose on account of its very low output resistance and linear input to output voltage over a wide range of input voltage. Since such a motor requires 6 or 12 V for full speed, depending on its type, an input resistor of 1000 to 3000 MΩ is required for normal sensitivity of detection. Although no resistor of more than 10,000 MΩ has been used for routine work, such a high value can be employed without adverse effect.

The second amplifying circuit with a voltage gain of four has a higher output resistance of about 500 Ω, and is suitable for use with a 12 or 24 V motor.

Both amplifiers supply a high voltage to the needle jet through a resistor of 1 MΩ.

VOLTAGE ATTENUATOR

Since several volts are produced at the output of either amplifier when an organic substance in the effluent stream burns, it is necessary to connect a voltage attenuator between the amplifier and the pen recorder.

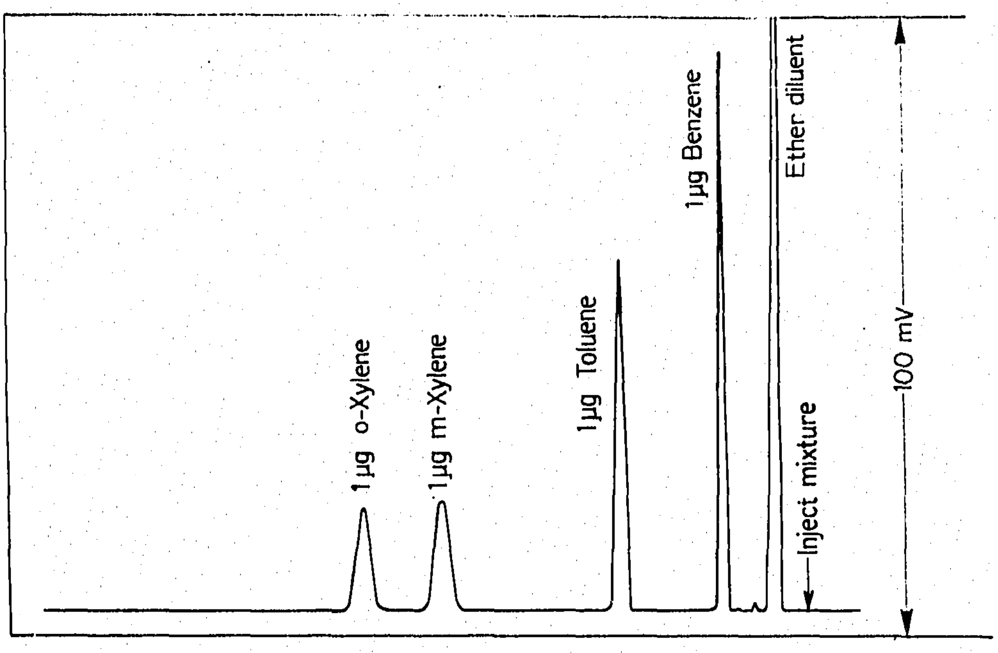

Fig. 5.

The attenuator circuits used with the amplifier are shown in Fig. 4. Small radio type switches are used. The odd and low value resistors are wound with insulated constantan wire. It is sometimes convenient to filter out A.C. by designing the attenuator to provide greater attenuation of A.C. than D.C., a feature of the second and third attenuator circuits.

References p. 154.

An amplifier constructed to the circuit shown in Fig. 2 was tested for noise level and sensitivity to voltage fluctuations in the supply mains. It was found that changes of + and — 5% resulted in output fluctuations of + and — 2 mV. With a constant mains voltage the short term drift was within 200 μV, and the maximum deviation after 4 hours was 500 μV.

The amplifier was connected to the detector shown in Fig. 1 and the chromatogram shown in Fig. 5 was obtained with a mixture of approx. 1 μg each of benzene, toluene, and *m*- and *o*-xylene. The initial large peak is 1 mg of ether used as a diluent.

Using the sensitivity parameter of DIMBAT, PORTER AND STROSS[3], the measured sensitivity of the benzene peak of Fig. 5 is $S = 1.1 \cdot 10^6$ ml·mV/mg, and the signal to noise ratio 200 to 1.

The column used was a coiled copper tube 4 m long and 4.5 mm internal diameter, filled with a stationary phase of "Apiezon L" grease on firebrick, operated at a temperature of 100° and an inlet pressure of 1426 mm of Hg. The carrier gas was hydrogen, flowing at a rate of 31 ml/min. The chart paper speed was 1.97 min/cm and the area of the benzene peak 4.0 cm^2.

ACKNOWLEDGEMENTS

The author wishes to thank Professor E. R. H. JONES for permission to publish this work, Messrs. L. J. GOLDSWORTHY AND C. S. G. PHILLIPS for their support, and Mr. F. HASTINGS for technical assistance.

SUMMARY

Multi-valve amplifying circuits for use with a gas chromatography flame ionization detector are described. With these amplifiers, designed to have a very high input and low output resistance and high degree of linearity between input and output, the detector exhibits high signal to noise ratio and sensitivity. The various possible causes of base line instability are discussed and the appropriate remedial measures indicated.

REFERENCES

1 I. G. McWILLIAM AND R. A. DEWAR, *Nature*, 181 (1958) 760; also a paper presented at the *2nd Symposium on Gas Chromatography*, Amsterdam, May 1958.
2 M. SCROGGIE, *Wireless World*, 58 (1952) 14, 89.
3 M. DIMBAT, P. E. PORTER AND F. H. STROSS, *Anal. Chem.*, 28 (1956) 290.

Received October 21st, 1958