FLAME IONIZATION DETECTORS

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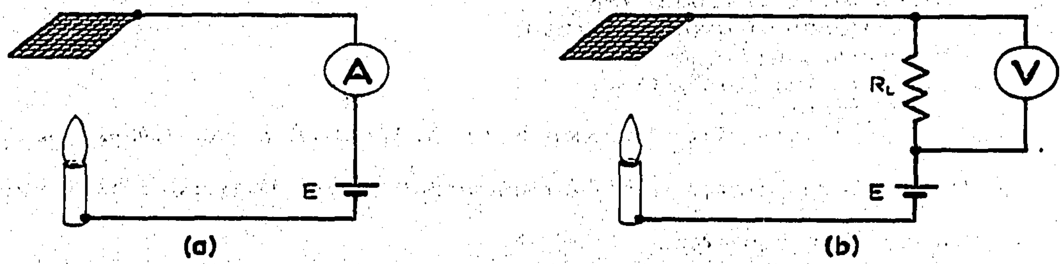
INTRODUCTION

One method of investigating food flavours involves the analysis of minute amounts of volatile materials in the air surrounding the food at its normal consumption temperature. Gas-liquid chromatography using flame ionization detection is a well-known method for this type of problem. This paper presents a discussion of the theoretical limits to the ultimate sensitivity and linearity of the flame ionization detector and describes methods for approaching these limits.

THE DIODE DETECTOR

(*a*) *Basis*

The flame ionization detector of McWilliam and Dewar[1] may be treated as a diode (Fig. 1a) with the collector as anode and the jet as cathode. To obtain the maximum linearity of the detector the current meter A should introduce negligible voltage drop in the circuit and have high sensitivity, negligible time constant and negligible drift. The usual method of measuring the ionization current is shown in Fig. 1b where the voltage drop across the load resistor R_L is measured with a high impedance voltmeter V. Electrometer amplifiers are commonly used for this purpose. Resistor R_L introduces an appreciable voltage drop with consequent non-linearity.



(a) (b)

Fig. 1. Basic diode measuring systems.

(*b*) *Voltage drop and non-linearity*

The manner in which this non-linearity arises may be seen from Fig. 2 which shows the ionization current obtained for different flow rates of ethylene as a function of the positive voltage applied to the anode of the detector. The sloping portion of the curves represents the region where the ion collection is not complete, while the horizontal plateau represents maximum collection efficiency. Load lines for $R_L = 0\,\Omega$, $10^9\,\Omega$, $10^{10}\,\Omega$ and $10^{11}\,\Omega$, are shown for an applied voltage E of 200 V. For $R_L = 10^{10}\,\Omega$ and an ethylene flow rate of 10^{-7} g/sec the voltage drop (RI) is 23 V and the voltage remaining across the detector ($E - RI$) is 177 V. Similarly, RI is 93 V and $E - RI$ is 107 V for an ethylene flow rate of $4 \cdot 10^{-7}$ g/sec. From Fig. 2 it can be seen that the voltage drop across the load resistor is proportional to the ethylene flow rate only if the load line intercepts the horizontal portion of the appropriate curve. As soon as the voltage across the detector falls below that required for complete collection of ions the output of the detector becomes non-linear. The linear region extends up to $5 \cdot 10^{-8}$ g/sec with $R_L = 10^{11}\,\Omega$, $5 \cdot 10^{-7}$ g/sec with $R_L = 10^{10}\,\Omega$ and to about $3 \cdot 10^{-6}$ g/sec with $R_L = 10^9\,\Omega$. At $R_L = 0\,\Omega$ the linearity extends to about 10^{-5} g/sec which is the limit of the inherent linearity of the detector for an applied voltage of 200 V.

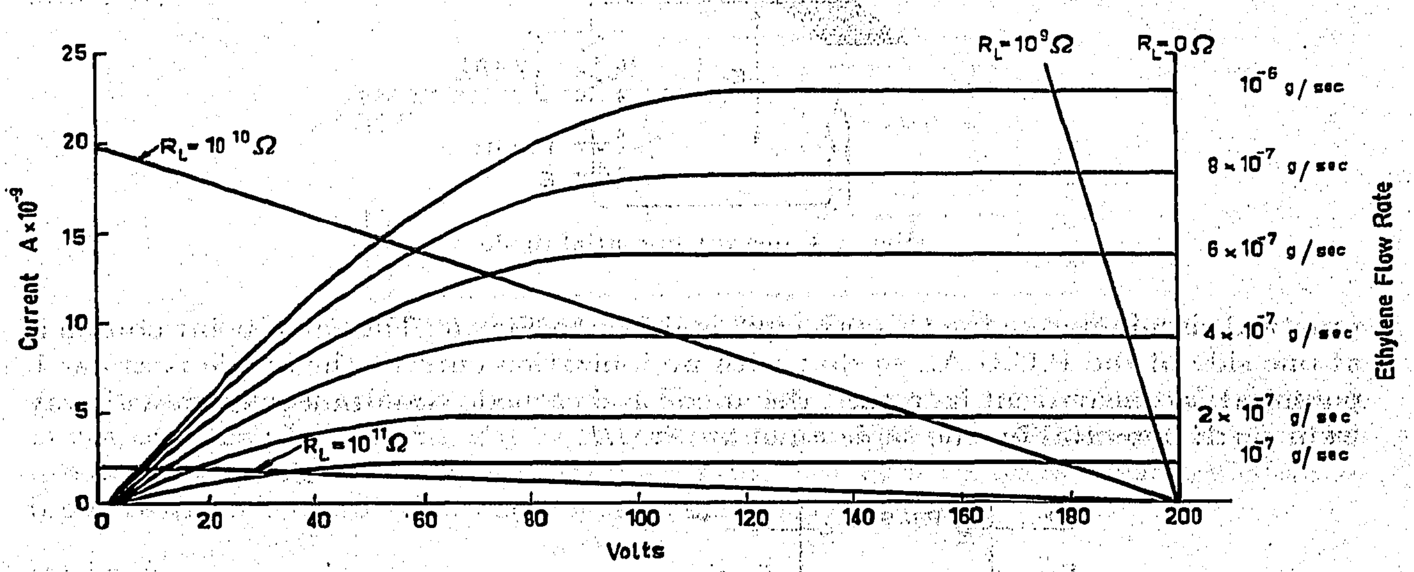


Fig. 2. Diode current curves.

In selecting a load resistor, a compromise must be made between the conflicting requirements of output voltage, which increases with increasing resistance, and linearity which decreases with increasing resistance. This difficulty is avoided if the applied voltage E is arranged to vary in such a manner that it always cancels the effect of the voltage drop in R_L. This is shown in Fig. 3 where an additional voltage E_1 is continuously adjusted to be equal to the voltage drop RI. Under these conditions the potential across the diode remains equal to E, independent of the ionization current. The effective load line then becomes $R_L = 0\,\Omega$, independent of the actual value of R_L. This permits a large output voltage to be obtained without this voltage being subtracted from the potential being applied across the diode.

Before discussing how this voltage E_1 is obtained in practice, it is necessary to consider the properties of a perfect unity gain amplifier (P.U.G.A.). Fig. 4a shows a diagrammatic representation of a P.U.G.A. Its three principal properties are (i) the ratio of output voltage to input voltage is very close to, but less than, unity (about 0.999), (ii) the input resistance is so high that the input current is negligible, (iii) the output impedance is negligible. If a P.U.G.A. is connected as in Fig. 4b, the effect produced is the same as shown in Fig. 3. The output voltage V of the P.U.G.A. is equal to the input voltage $V = RI$ and is connected so as to oppose it; consequently the output voltage is equivalent to E_1 of Fig. 3 and the voltage across the diode will remain at E volts. Note that any point on this circuit may be earthed. A typical practical circuit employing this principle is shown in Fig. 4c. The earth point chosen is at one side of the P.U.G.A., so that with no ionization current the anode is at earth potential; as the current increases, the anode and cathode simultaneously move away from earth potential by the same amount *viz.* RI.

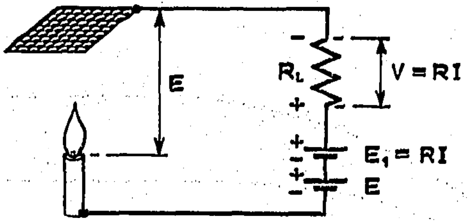


Fig. 3. Constant potential diode.

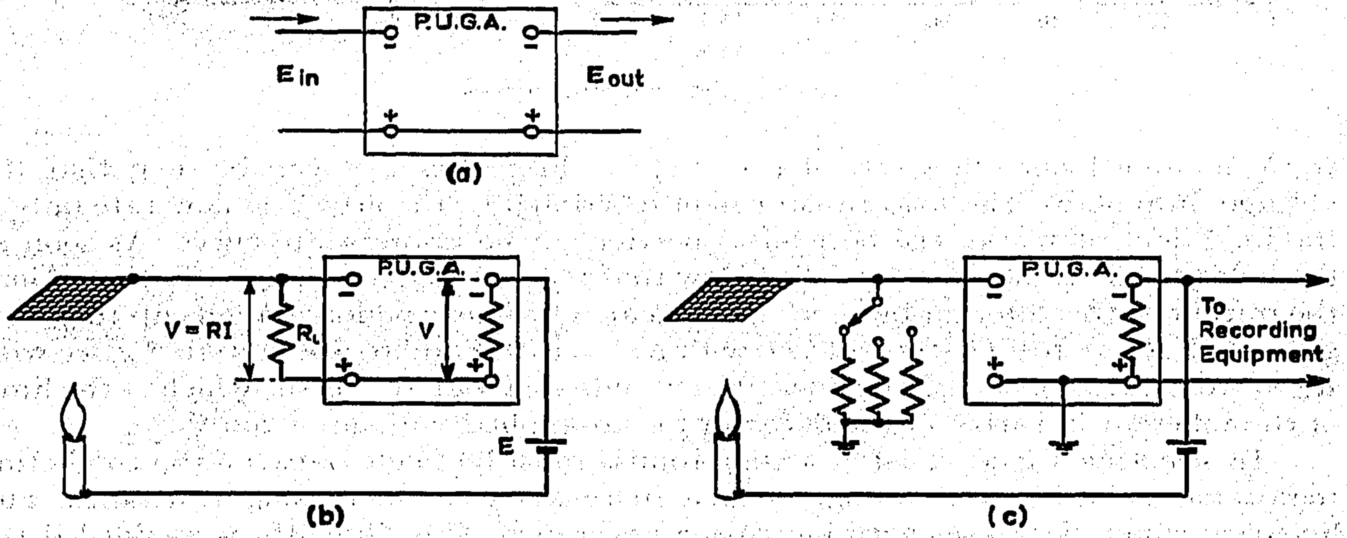


Fig. 4. Constant potential diode.

(*c*) *Time constant*

The connection from the anode of the detector to the input of the P.U.G.A. (or in fact, any amplifier or electrometer) has a capacitance C to earth. It is usual to use a coaxial cable for this connection and a typical value of C for 60 cm of cable is 40 pF ($40 \cdot 10^{-12}$ F). If there is an increase in the ionization current this capacitor charges up. The time constant τ, which is the time required to charge this capacitor to 63 % of its final value, is given by $\tau = R_L C$. If $R_L = 10^{10}\,\Omega$ and $C = 40 \cdot 10^{-12}$ F then $\tau = 0.4$ sec; for $R_L = 10^{11}\,\Omega$, $\tau = 4$ sec; and for $R_L = 10^{12}\,\Omega$, $\tau = 40$ sec. The time required to charge to 99 % of final value is about $5\,\tau$ so that the use of high value resistors, even with low capacitance cable, leads to inadmissibly long time constants. The time constant of the input circuit can be reduced by a large factor if the shield of the coaxial cable is connected not to earth, but to the output of the P.U.G.A., as in Fig. 5. Now, the effective capacitance $C_{eff} = C\ (1 - \text{gain})$ and for a gain of 0.9996*; $C_{eff} = 0.0004\ C$. Hence $\tau = 0.2$ msec for $R_L = 10^{10}\ \Omega$, $\tau = 2$ msec for $R_L = 10^{11}\ \Omega$ and $\tau = 20$ msec for $R_L = 10^{12}\ \Omega$. Since the cathode of the diode is also connected to the output through battery E the anode–cathode capacitance is also reduced by a factor of 0.0004.

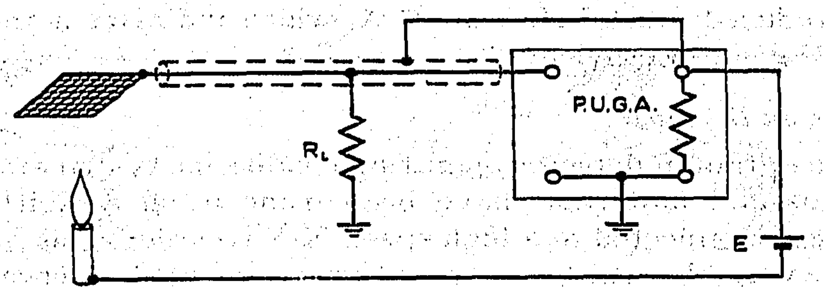


Fig. 5. Reduction of time constant; cancellation of cable capacitance.

If the self capacitance of resistor R_L is not negligible, it is also reduced by a factor of 0.0004 by returning it to the output of the P.U.G.A. However, the effective resistance is now given by $R_{eff} = R_L\ (1 - \text{gain})^{-1} = 2500\ R_L$, so to obtain an effective input resistance of $10^{12}\ \Omega$ an actual resistor of $4 \cdot 10^8\ \Omega$ is used.

(d) *Drift*

The design of the P.U.G.A. employs a considerable amount of negative feedback, which means high stability can be achieved and drift rates can be as low as 2 % of full scale per hour, which is adequate for many gas chromatographic applications.

(e) *Limit of detection of diode*

The sources of noise which set the final limit of detection of the diode are:

(1) *Chemical noise in the flame.* This arises from stationary phase eluting from the column and from impurities present in the carrier gas, hydrogen and air.

(2) *Physical noise in the flame.* The ionization current consists of discrete charged particles which arrive at the anode in a random fashion, producing what is known as "shot" noise. The root mean square value of the shot noise current is given by $i_{RMS} = \sqrt{3.2 \cdot 10^{-10}\ I\ \tau^{-1}}$ A where I = D.C. current in A and τ = time constant in sec. The noise voltage produced across the load resistor is $E_{RMS} = I_l\ \sqrt{3.2 \cdot 10^{-19}\ I\ \tau^{-1}}$ V. For $R_L = 10^{12}\ \Omega$, $\tau = 1$ sec and $I = 10^{-11}$ A (typical value of the ionization current produced by commercially pure gases), $E_{RMS} = 1800\ \mu$V approximately.

(3) *Physical noise in the load resistor.* At room temperature the Johnson noise in the load resistor is given by $e_{RMS} = 1.29 \cdot 10^{-10}\ \sqrt{R_L\ \tau^{-1}}$ V. For $R_L = 10^{12}\ \Omega$ and $\tau = 1$ sec, $e_{RMS} = 129\ \mu$V.

(4) *Amplifier noise.* Noise is generated in the first valve of the P.U.G.A. (or any amplifier) due to grid and plate currents. With careful design this noise can be kept to about 300 μV (R.M.S.).

If chemical noise is disregarded, shot noise sets the limit of detection. For a

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* See "Measurements", section (*f*).

background current of 10^{-11} A the corresponding shot noise current is $1.8 \cdot 10^{-15}$ A (R.M.S.) which corresponds to an ethylene flow rate of 10^{-13} g/sec approx. If a signal to noise ratio of unity is selected the limit of detection would be 10^{-13} g/sec of ethylene.

In practice, using commercially pure hydrogen and nitrogen, it is possible to attain such a background current. If further purification of these gases reduces this background current to 10^{-12} A the shot noise only decreases by $\sqrt{10}$ and the limit of detection is then $3 \cdot 10^{-14}$ g/sec of ethylene. It seems unlikely that the ionization current can be reduced much below 10^{-13} A, which indicates a theoretical limit of detection of 10^{-14} g/sec of ethylene.

(*f*) *Measurements on the diode*

To determine the optimum detector operating conditions, systematic changes in each of the dimensions and flow rates have been made using a Keithley Model 150A Micromicroammeter connected to a high speed X-Y recorder. This method eliminates the drifts in these variables which can occur between manual observations. A stainless steel tube 0.5 m long × 4.5 mm bore packed with 40–60 acid washed celite is used as a flow resistance between the sample introduction and the detector. Nitrogen (50 ml/min) is passed through the column and ethylene is metered into it as required. Hydrogen (50 ml/min) is added to the column effluent and the mixture burns at a tapered platinum–20% rhodium jet having an 0.325 mm orifice (see Fig. 8). The anode consists of a disc of 1 cm dia. platinum gauze (48 mesh) situated 1 cm above the jet. An airflow of 1 l/min is maintained through the detector. A load resistor of 10^{12} Ω is used and the detector output signal is connected via a guarded coaxial connector to a Halex 302E Electrosensor* used as a P.U.G.A. This P.U.G.A. has a gain of 0.9996, input impedance of 10^{17} Ω and output impedance of 0.3 Ω. The output of the P.U.G.A. is attenuated and then recorded with a Speedomax Model G, one second recorder**. Using commercially pure gases a background ionization current of 10^{-11} A is obtained, the associated noise being 10^{-14} A (R.M.S.). Since the shot noise for 10^{-11} A is only $1.8 \cdot 10^{-15}$ A (R.M.S.) it appears that the chemical noise in the flame is the limiting factor setting the present practical limit of detection at $5 \cdot 10^{-13}$ g/sec of ethylene. The drift rate under these conditions is the equivalent of 10^{-11} g/sec ethylene/h.

THE FLAME IONIZATION TRIODE

(*a*) *Basis*

To reduce the drift rate of the D.C. amplifying system associated with the diode, an A.C. system and the flame ionization triode have been developed[2].

Fig. 6a shows the basic triode in the grounded cathode configuration. An alternating voltage is applied between the grid and the cathode and the resultant alternating plate current flows through load resistor R_L producing an alternating voltage at the output; R_L has values similar to those in the D.C. system. The time constant of the input circuit must be small compared with the time for one cycle of the A.C. used, so capacitance effects are of great importance. Fig. 6a shows the capacitances associated with the components of the detector. Since the grid has a large A.C. signal on it, some A.C. will be fed directly to the anode via the large capacitance C_2. To

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* Halex Inc., California, U.S.A.

** Leeds and Northrup Co., Philadelphia, Pa., U.S.A.

avoid this the grounded grid configuration of Fig. 6b is used, in which the A.C. is applied to the cathode and the feedthrough to the plate is via C_1. The screening effect of the earthed grid makes C_1 several orders less than C_2. Since the capacitance C_3 is directly across the transformer, it has no effect on the system. However, as C_3 is between anode and earth this adds to the stray capacitances which, in association with R_L, set the time constant of the system. For convenience 50 c/s is chosen as the operating frequency, so the time constant must be less than 10 msec, consequently capacitance reduction must be employed. Fig. 6c shows how the P.U.G.A. may be used to keep the grid-anode voltage constant and hence reduce the effective value of C_2 to about 10^{-2} pF. C_1 is already reduced to 10^{-3} pF by the presence of the grid.

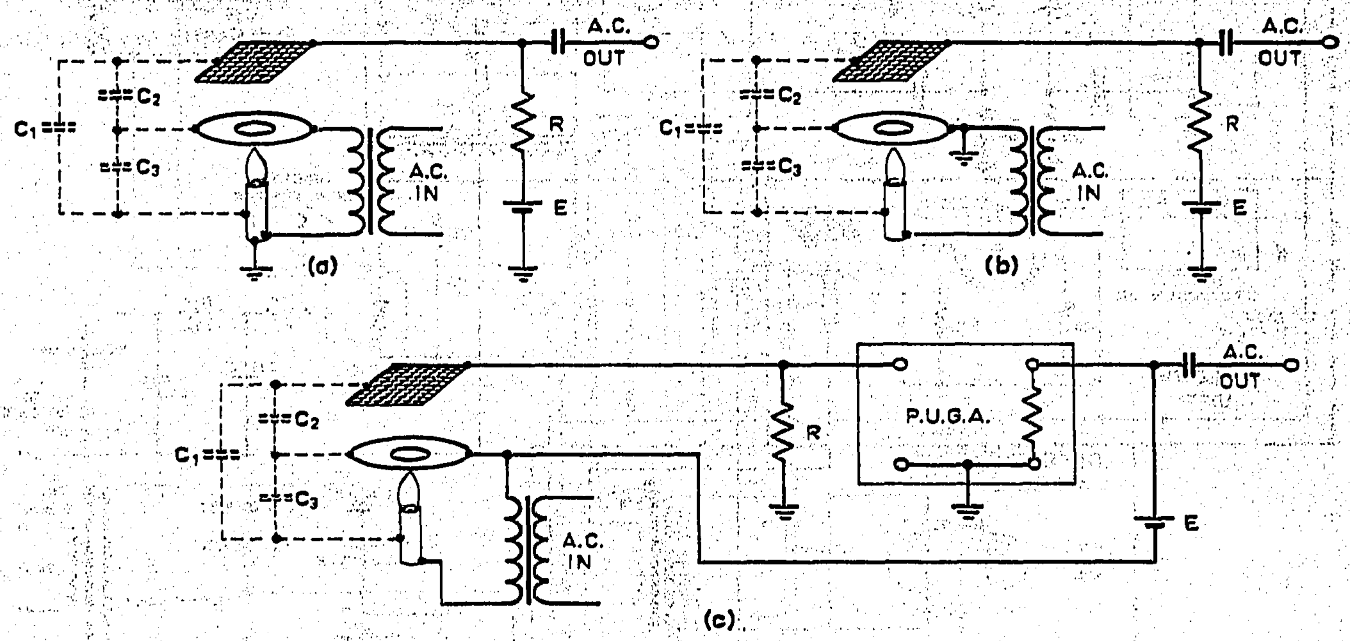

Fig. 6. Flame ionization triode.

The A.C. output of the P.U.G.A. is fed through an attenuator to a combined A.C. amplifier and phase-sensitive detector (Fig. 7). The amplifier follows normal practice; 0.05 μF capacitors tune the signal and reference transformers to 50 c/s. The neon Ne2 conducts as soon as the voltage across the signal transformer exceeds 60 V. By this means the D.C. output to the 10 mV recorder is linear to about 14 mV but is sharply limited at 15 mV. A Bristol Syncroverter used as a phase-sensitive detector has negligible drift compared with valve and transistor systems. Any residual feedthrough via the cathode-plate capacitance is removed by applying an out-of-phase voltage to C_0; however, this capacitance is kept small since its use increases the input time constant.

(b) *Linearity*

The considerations of the inherent linearity of the diode detector apply also to the triode and Fig. 6c may be considered as the A.C. equivalent of Fig. 4c. The effective load resistor R_L is zero, independent of the actual value of R_L.

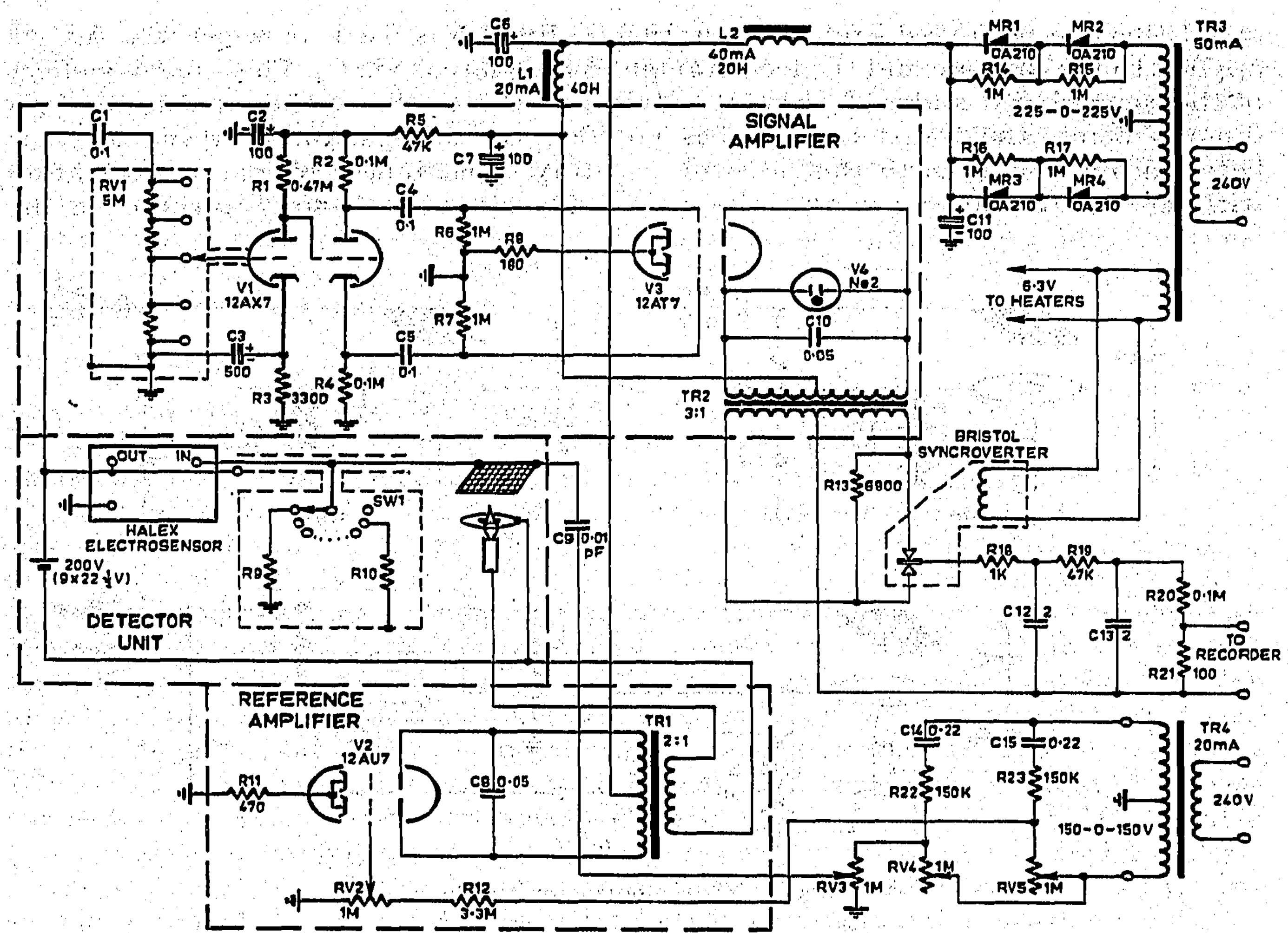

Fig. 7. Amplifier for flame ionization triode.

(c) Time constant

The time constant associated with the input to the P.U.G.A. sets a limit to the maximum frequency at which the system can be operated. For a total effective input capacitance of 10^{-2} pF and a load resistor of $10^{12}\,\Omega$ the input time constant is 10^{-2} sec which permits the use of frequencies up to 50 c/s. The time constant of the overall system is set by the integration time of the R.C. network following the phase-sensitive detector (Fig. 7). To provide satisfactory integration of the output of the phase-sensitive detector this time constant is somewhat greater than 0.2 sec.

(d) Drift

As the D.C. output voltage is independent of the D.C. conditions of the P.U.G.A., the major source of drift is eliminated. Some long-term drifts are caused by changes in the feedthrough capacitances due to changes in dimensions of the detector; variations in the cancelling voltage can also occur.

(e) Limit of detection of triode

The sources of noise in the triode are the same as those in the diode and similar considerations apply to their magnitudes. For an overall time constant of 1 sec, the shot noise is 1800 μV (R.M.S.) for a background current of 10^{-11} A. The magnitude of this noise can be reduced by increasing the integration time of the network after the phase-sensitive detector but only at the cost of increased time constant of the whole system. For equivalent time constants the diode and triode detectors have the same limit of detection.

(*f*) *Measurements on the triode*

Fig. 8 is a diagram of the flame ionization triode used in these measurements. It consists of the basic diode with the addition of an annular grid. An analysis of variables, similar to that undertaken for the diode, has shown that optimum conditions for the diode and triode are similar. The size and position of the grid are shown in Fig. 8.

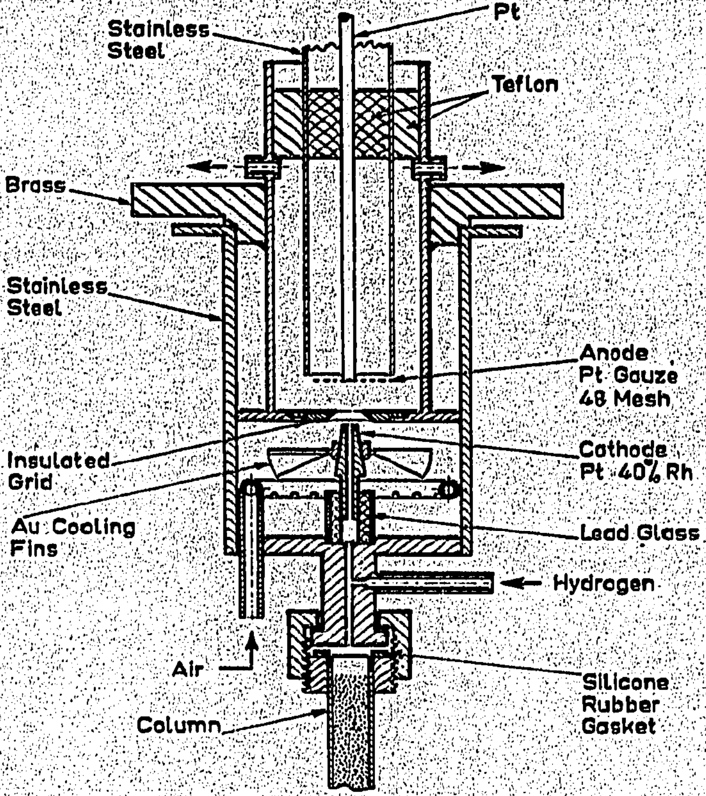

Fig. 8. Flame ionization triode.

The drift rate (with a $10^{12}\,\Omega$ load resistor) is less than 10 μV/h, which is equivalent to 10^{-15} g/sec ethylene/h and is an improvement of four orders of magnitude over the diode. The electronic noise is again about 300 μV (R.M.S.) which is negligible as compared with the shot noise (1800 μV) in the background ionization current. The overall electronic noise is negligible compared with chemical noise in the flame.

CONCLUSION

Using the methods and circuits which have been described it is possible to approach the inherent limits of linearity and detection of both the diode and triode flame ionization detectors.

Linearity over a range of $10^8:1$ is possible. The major theoretical noise contribution is due to the shot effect in the background ionization current of the hydrogen flame. For a background current of 10^{-11} A, obtained from commercially pure gases, the theoretical limit of detection is 10^{-13} g/sec of ethylene using a bandwidth of 1 c/s. Chemical noise due to impurities in the gases used sets the present limit of detection at about $5 \cdot 10^{-13}$ g/sec of ethylene.

The diode and the triode detectors have the same noise limitations but the drift of the diode D.C. system is approximately 100 times its theoretical noise level (peak to peak) per hour, whereas the drift of the triode is negligible. The drift rate produced by stationary phase elution from some types of columns can be greater than that due to the diode electronic system and, under these circumstances, there is little to be gained by using the triode system.

SUMMARY

Methods are described for improving the performance of the amplifiers associated with the diode and triode flame ionization detectors. The effect of these amplifiers on linearity, time constant and drift rate is discussed together with the theoretical and practical limitations of detection.

REFERENCES

[1] I. G. McWilliam and R. A. Dewar, in D. H. Desty (Editor), *Gas Chromatography*, Butterworths, London, 1958, p. 142;
I. G. McWilliam, *J. Chromatog.*, 6 (1961) 110.
[2] J. Middlehurst and B. H. Kennett, *Nature*, 190 (1961) 142.