

# A PROTECTED RADIOACTIVE SOURCE FOR ELECTRON CAPTURE AND OTHER GAS CHROMATOGRAPHIC DETECTORS

N. L. GREGORY

*National Institute for Medical Research, Holly Hill,  
Hampstead, London (Great Britain)*

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## INTRODUCTION

In electron capture detectors so far described<sup>1,2</sup>, tritium has been used as the primary source of ionisation. Tritium is chosen because the 0-8 kV  $\beta$ -particles emitted from a tritium source ionise the gas within the detector only through a range extending a few millimetres from the source. It is thus possible to make detectors in which ion pair formation occurs only within a small region close to the source, which is used as the cathode, and all the secondary electrons so formed travel the whole width of the detector before being collected at the anode. This situation is desirable in an electron capture detector because it combines maximum sensitivity with minimum secondary effects, *e.g.* peak inversion due to direct ionisation of the sample by radiation from the radioactive material.

However, the use of tritium sources has the disadvantage that the tritium-bearing compound used cannot be protected by sealing between metal foils without preventing the egress of  $\beta$ -particles. The radioactive material is thus open to attack from any reactive compound carried in the gas stream from the column. It is also susceptible to progressive deterioration due to the deposition of films of stationary phase, etc., stripped from the column. At temperatures above 200° there is loss of tritium from the source compound even in the absence of reactive compounds in the gas stream<sup>3</sup>. The use of detectors employing tritium sources is thus subject to certain limitations and some of these limitations apply also to other detectors in specific circumstances.

By using the technique described in this paper, the advantages normally associated with tritium can be obtained whilst using other, more stable sources and, in addition, the source material is protected from contact with the carrier gas stream from the chromatograph column. This is accomplished by enclosing the source within an additional chamber separated from the normal detector chamber. The source chamber is then maintained free from unwanted compounds by "scavenging" it with a stream of clean gas. The required ionisation in the detector chamber is secured by electrons passing from the source chamber into the main chamber under the influence of a suitable electrical field. Thus the two processes normally taking place in the detector, *viz.* the generation of an electron current by ionisation from the radioactive source and the subsequent electron impact processes leading to detection of the compounds carried from the column, are separated. This eliminates subsidiary effects resulting

from direct ionisation of the sample compound by primary radiation from the radioactive source, one of the causes of peak inversion in electron capture detectors. Moreover as the electron stream can be led into the main chamber in a specific region whatever radioactive material is used, there is a greater freedom of choice of radioactive material, and tritium need no longer be used.

#### APPLICATION TO ELECTRON CAPTURE DETECTORS

The application of this principle to an electron capture detector is illustrated in Fig. 1.

A stream of carrier gas from a chromatograph column is introduced into the detector chamber (B) through the gauze anode (A) in the normal way<sup>1</sup>.

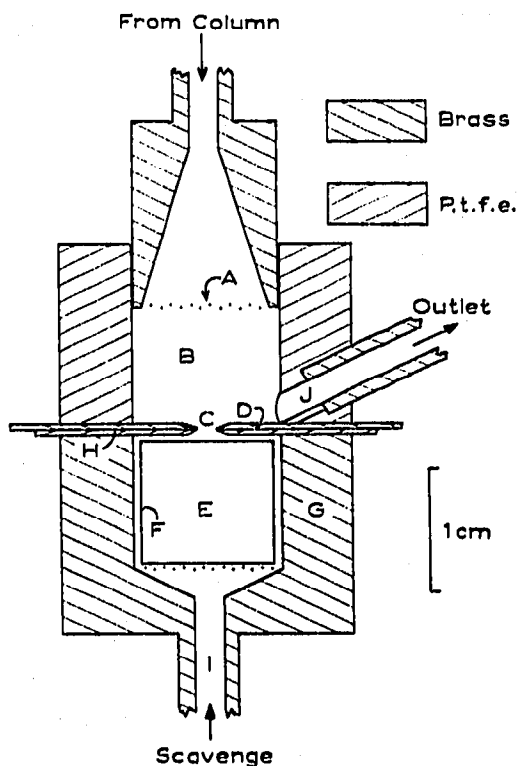


Fig. 1. Electron capture detector with an external radiation source.

Electrons generated in the cavity (E) by the radioactive source (F) diffuse through the hole (C) in the metal plate (D) under the influence of an electric field which is provided by a potential applied between the metal block (G) and the plate (D). The plate (D) is insulated from the block (G) by a thin P.T.F.E. sheet (H).

The electron current between the plate (D) and the anode (A) is recorded and used to indicate the presence of compounds in the carrier gas stream.

The source chamber (E) is kept free of contaminants by a separate flow of clean carrier gas entering via the pipe (I), which passes into the main chamber (B) through the hole (C). The exit from the detector chamber (B) is through the pipe (J).

## EXPERIMENTAL

A detector was constructed as shown in Fig. 1, with an  $18 \mu\text{C } ^{226}\text{Ra}$  source. For calibration purposes it was mounted in an oven at the output of a gas chromatograph employing a 4 ft. packed column of 4 mm I.D., and a gas density balance detector<sup>4</sup>. Provision was made for diluting the gas stream leaving the density balance before it entered the electron capture detector. The carrier gas used was nitrogen.

The variation of current through the detector with changing bias voltages applied to the source, between (G) and (D), is shown in Figs. 2a and 2b, which are

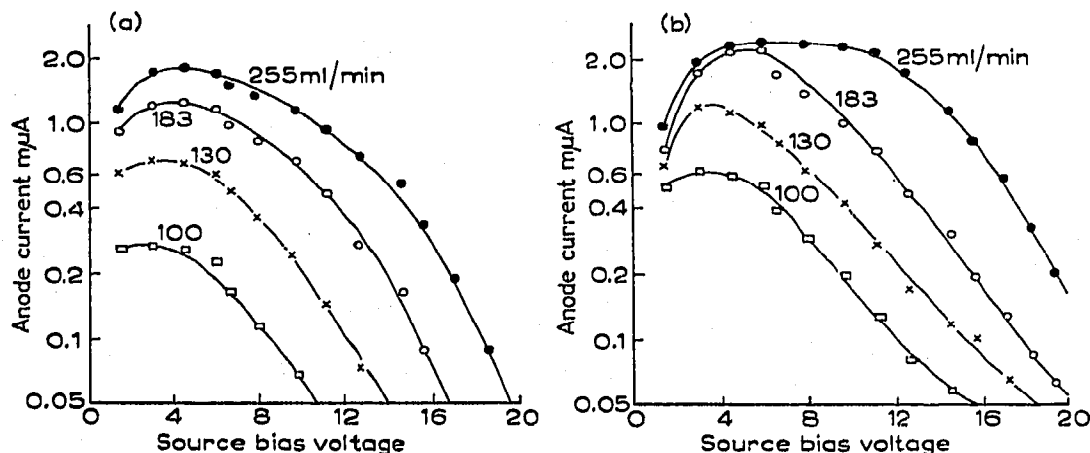


Fig. 2. Anode current *versus* source bias voltage with differing scavange gas flow rates: (a) anode voltage = 4.5 V; (b) anode voltage = 9 V.

plotted with different collector voltages applied between the anode (A) and the cathode (D) of the detector chamber. The different curves in each figure were obtained with different scavange gas flow rates.

Figs. 3a and 3b show the variation of electron current with changing collector voltage with two different rates of gas flow, and with various bias voltages applied to the source chamber.

The working conditions selected for stable operation were with the source bias

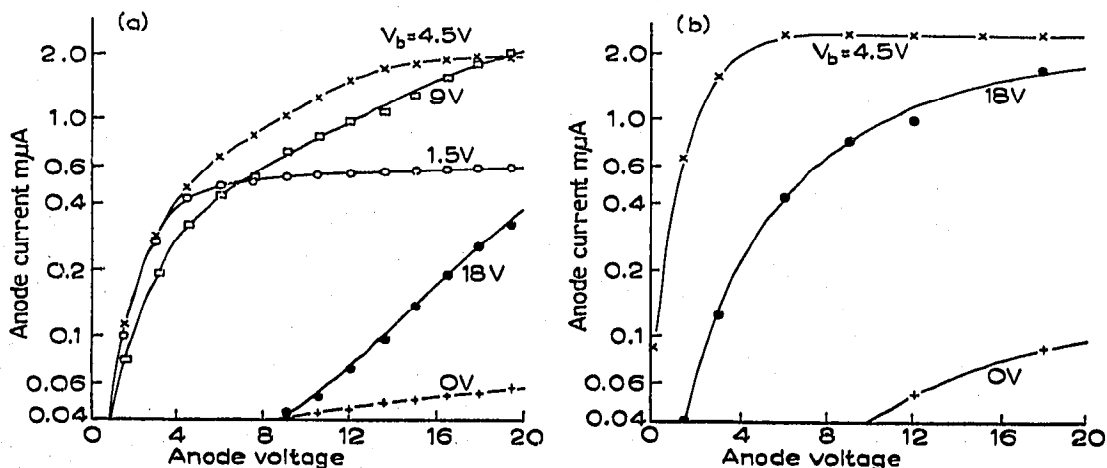


Fig. 3. Anode current *versus* anode voltage with differing source bias voltages: (a) scavange gas flow = 130 ml/min; (b) scavange gas flow = 255 ml/min.

voltage set at 6–9 V, the detector anode voltage in the range 3–15 V and a scavenge gas flow rate of 180–250 ml/min. For optimum conditions at a temperature of 245° the source and detector voltages used have both been 6 V, with a scavenge gas flow of 180 ml/min and a carrier gas input from the column of 60 ml/min. A representative sample concentration *versus* detector current curve is given in Fig. 4. The sample concentrations plotted in the curve were derived from the gas density balance output,

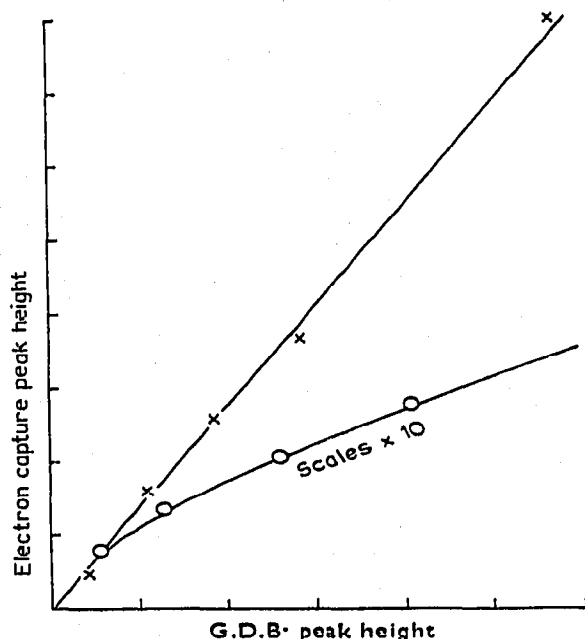


Fig. 4. Detector linearity. Electron capture peak height *versus* gas density balance peak height. Detector temperature: 67°; scavenge gas flow: 180 ml/min; total gas flow through detector outlet: 210 ml/min; anode voltage: 6 V; source bias voltage: 6 V; inter-detector dilution ratio = 1,500:1.

the dilution factor between the two detectors being of the order of 1,500\*. The response is approximately linear with peak current changes of the order of 20% of the standing detector current. In analytical work, where peak areas are of more interest than the electron capture at peak sample concentration, the detector calibration in terms of area is linear to the same degree over the same range of peak heights.

#### DISCUSSION

The curves of Fig. 3 show that as expected, electron flow from the source chamber (E) into the detector chamber (B) is controlled by the direct effect of the applied field in the detector chamber as well as the bias voltage applied between the plate (D) and the source chamber (G). The source chamber (G) may be regarded as a cathode and the plate (D) as a subsidiary anode competing with the detector anode (A) for the available electrons. The curves also show that the gas flow rate has a strong influence on the electron current. As electron drift velocities are orders of magnitude greater than the gas flow velocity (see *e.g.* ref. 5), gas flow cannot influence electron flow directly. This implies that the electron flow is largely influenced by the presence of relatively slowly moving ions in the gas stream. The common assumption that current

\* A method for making large, stable dilution ratios is to be published.

in such detectors is carried by free electrons rather than by negative ions has been confirmed in this laboratory (unpublished work). Thus it is probable that the effect of gas flow rate is concerned with movement of the positive ions which are created in the source chamber by the radiation from the radioactive source.

This movement of positive ions can influence the electron current in two ways, (i) by dispersing the positive ion space charge left in the source chamber by the withdrawal of electrons and (ii) by a process of "ambipolar diffusion" (see *e.g.* ref. 6), *i.e.* positive ions are carried by the gas stream from the source chamber into, or towards, the detector chamber (B) against the applied field. As electrons are attracted towards the positive ions their movement from the source into the detector is facilitated by the flow of scavenge gas. The process may well influence the relative collection efficiencies of the two "anodes" (A) and (D).

In short, the electron current through the detector depends on the two applied voltages and upon the gas flow rate and the actual current observed is the result of a balance between a number of different processes. It can be seen, however, that it is possible to choose a working point at which the current is not critically dependent on any one variable. Thus stable operation can be secured.

The mechanism of the external source is obviously rather complex and, in its present form the gas flow rates necessary for its successful operation are larger than the carrier gas flow through average analytical columns. They are not, however, so large as to dilute unduly the sample entering the detector, when working with packed columns. Indeed, it has been found convenient to use additional dilution between the column and the detector and it is probable that when working with specific compounds for which electron capture detectors have high sensitivity, it could be used in its present form with capillary columns.

It is possible that a considerable reduction in the scavenge gas flow could be made if the source chamber were redesigned in such a way as to increase the effectiveness of the source bias voltage; perhaps an additional "pusher" electrode could be used. Also little attention has been paid to the size of the hole (C) through which the electrons are transferred, and to the thicknesses of the plate (D) and its insulator (H). These factors may each be expected to influence the efficiency of transfer of electrons from the source chamber to the main chamber and the dependence of electron current on gas flow rate.

With small collecting voltages applied to the anode, the linearity of the detector is of the same order as that of other electron capture detectors, and the use of these small collecting voltages ensures that the small fields in the detector under these conditions do not materially increase the energy of the electrons in the chamber. Thus one factor which can introduce anomalies in detector sensitivities is eliminated.

When using higher collecting voltages the detector response may be anomalous at low sample concentrations. The use of pulsed voltages has shown that the anomalous response is a function of mean current through the chamber rather than of the applied voltage, and that time constants of the order of seconds are involved. This implies that space charges, or surface charges, are of great importance in the operation of the detector. Different and possibly better performance may therefore be expected with a source of size different from the 18  $\mu\text{C}$  adopted here, and with detectors designed to minimise the effects of surface charges.

## APPLICATION TO ARGON DETECTORS

The same type of external source may be used with a normal argon detector anode<sup>1</sup>, e.g. as in Fig. 5. One source can in fact be used with interchangeable anodes to form a dual purpose detector.

The advantage of an external source used in this way with an argon detector is the relative immunity of the radioactive source to deterioration resulting from contact with corrosive samples or stationary phase bleeding from the column.

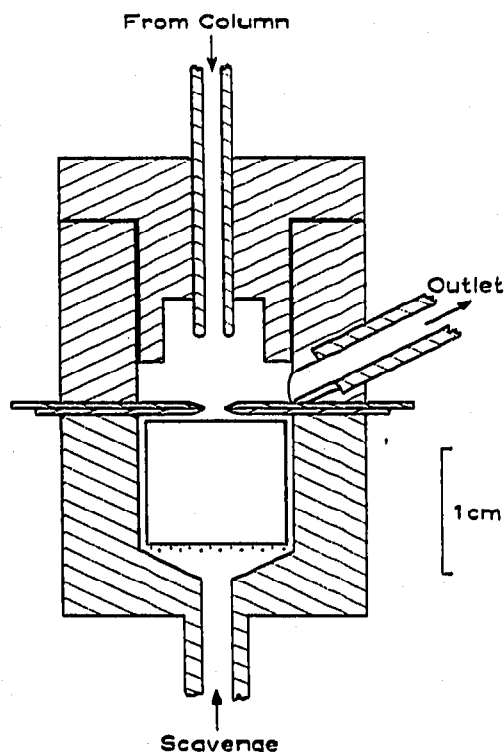


Fig. 5. Argon detector with an external ion source.

Such a detector was tried, and was found to produce an apparently normal response, but no data as to detector linearity was obtained. As the source size is significant in the performance of argon detectors, and as the source characteristics are not the same with argon as with nitrogen as a scavenge gas, further development work would be required to produce an argon detector of optimum performance.

## CONCLUSION

The technique described for isolating the radioactive source in ionisation detectors has been shown to be practicable in the case of electron capture detectors, and to make possible the safe use of such detectors at higher temperatures than would be reasonable when using the more usual tritium sources. The upper limit of temperature is now set by the constructional materials used; the detector described has operated satisfactorily for some months at 250°.

Indication has also been obtained that the technique could be applied successfully to argon detectors. The radiation sources in these detectors can thus be protected

from the adverse action of compounds leaving the column. The technique makes practicable a valuable extension of the application of ionisation detectors in gas chromatography.

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#### SUMMARY

By use of the technique described, ionisation detectors can be constructed in which there is no contact between the radioactive source and compounds eluted from the chromatograph column. This has advantages:

1. In electron capture detectors where it makes the use of radioactive materials other than tritium convenient. Higher operating temperatures may therefore be used.
2. In situations where eluted compounds might otherwise lead to deterioration of the radioactive source.

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