

THE DETECTION OF TRITIUM LABELLED COMPOUNDS IN VAPOUR PHASE CHROMATOGRAPHY

HORACE E. DOBBS

*U.K. Atomic Energy Authority, Isotope Research Division,
Wantage Radiation Laboratory, Wantage, Berks. (Great Britain)*

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INTRODUCTION

In recent years a variety of methods have been developed for the preparation of tritium labelled compounds¹⁻⁷. In those methods that employ exchange and irradiation techniques the desired tritiated compound is almost invariably accompanied by tritium labelled impurities^{8,9}, and rigorous purification and analysis is essential in most cases to ensure that the product is *radiochemically* pure. Vapour phase chromatography has proved a very useful technique both for the purification and the analysis of labelled compounds. In vapour phase chromatography it is desirable to measure continuously the activity of the gas coming from the column to avoid the misleading results that may be obtained by condensing fractions and measuring their activities individually. The low maximum energy (18 KeV) of tritium β particles prohibits the use of end window counters that can be used for detecting β particles with higher energies such as those from carbon-14^{10,11}. Suitable detectors which may be used with tritium are discussed below.

SCINTILLATION AND PROPORTIONAL DETECTORS

LOWE AND MOORE^{12,13} have used a liquid scintillation technique for measuring ¹⁴C-labelled vapours from a gas-liquid chromatography column; the same method can also be used for detecting tritium labelled compounds¹⁴. FUNT AND HETHERINGTON¹⁵ used a hollow plastic scintillator in the form of a spiral for measuring ¹⁴C in the gas phase and CAMERON, BOYCE AND TAYLOR¹⁶ have used a similar plastic scintillator in the form of a hollow cylinder (volume about 0.5 c.c.) for detecting tritium in a flowing gas.

WOLFGANG AND ROWLAND¹⁷ have developed a gas flow proportional counter that can be used at temperatures up to 200°. In their method methane is injected into the gas stream to make a suitable "counting" gas after it has passed through a thermal conductivity mass detector, and the mixture fed into a specially designed gas flow proportional counter.

IONISATION CHAMBER DETECTOR

A gas flow ionisation chamber can be used as a high temperature detector^{18, 20} and this paper describes a chamber that has been used at temperatures up to 190°.

The maximum current that can be measured in an ionisation chamber is given by:

$$I = \frac{N \cdot E \cdot e}{w}$$

where I = current (amp.)

N = number of disintegrations per second

E = average energy per disintegration (electron volts)

w = number of electron volts required, to produce one ion pair in the gas.

This varies with the nature of the gas in the cell; for air the value is 32.5 eV and for argon it is 27.8 eV¹⁹.

e = electronic charge (coulombs)

For 1 μ C of T gas in an ionisation chamber filled with argon, the maximum current due to the T is about $1.2 \cdot 10^{-12}$ amp. This theoretical ionisation current will not be obtained in practice due to absorption of the β particles in the chamber walls. The proportion of β particles lost by this effect is reduced by increasing the size of the cell, thus its dimensions are determined by compromising the increase in efficiency obtained by increasing its size with the decrease in chromatographic resolving power.

EXPERIMENTAL

A design that has been used in this laboratory for detecting tritiated water in a gas flow at temperatures up to 190° is shown in Fig. 1. Several designs for the central collecting electrode were tested but the concentric steel rod shown in the diagram proved to be the most efficient. The chamber (volume 3.0 c.c.) was connected to the amplifier by a length of screened co-axial Teflon cable fitted with a jockey adaptor.

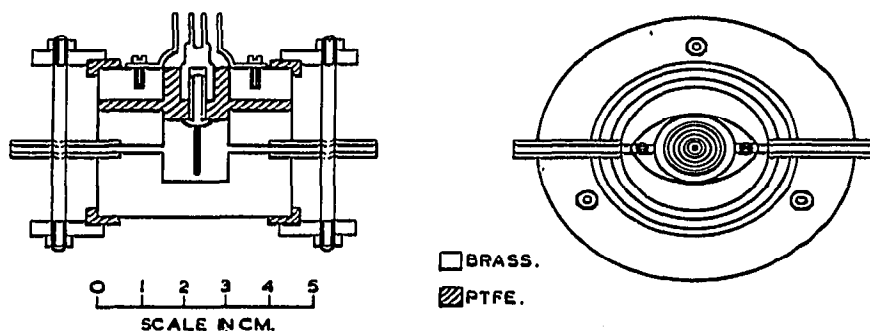


Fig. 1. A gas flow ionisation chamber for use at high temperatures.

To determine the characteristics of the design, the ion chamber was housed in an oven and connected to a D.C. amplifier (A.E.R.E. type 1388B); all experiments were carried out using the minimum time constant setting. The amplifier was

connected to a Honeywell Brown recorder and the voltage to the cell was supplied by dry batteries. The efficiency of the ionisation chamber was tested using the arrangement shown schematically in Fig. 2. The gas flow rate was determined by a calibrated flow meter (Rotameter) and tube T contained tritiated water of known

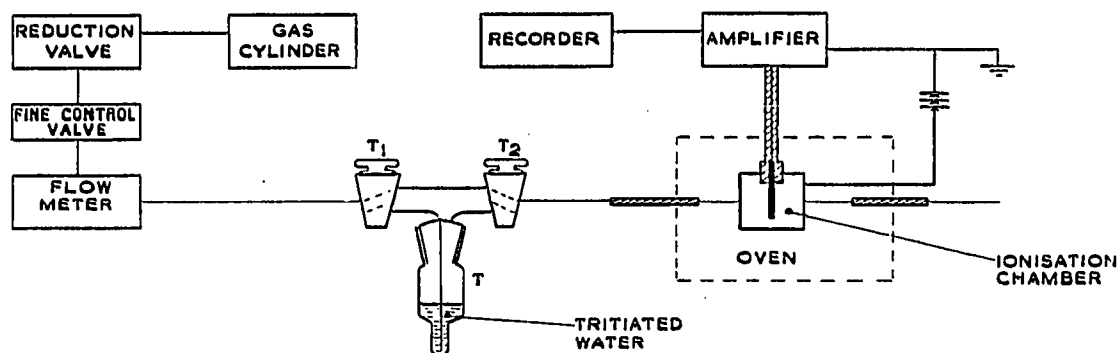


Fig. 2. The arrangement used for determining the characteristics of the ionisation chamber

specific activity. By turning taps T_1 and T_2 simultaneously the stream of gas of predetermined flow rate was bypassed through the water for any desired period thus becoming saturated with water vapour and delivering a known amount of tritium to the chamber. To prevent variations of the vapour pressure of the tritiated water, T was immersed in a thermostated water bath. The gas after bubbling through T was shown to be saturated with tritiated water vapour by condensing out several fractions in a liquid nitrogen trap and counting them individually in a calibrated liquid scintillation counter. The measured count rates agreed with calculated values.

RESULTS

The graph (Fig. 3) was obtained by measuring the peak heights on the recorder chart produced by passing nitrogen (flow rate 0.1 l/min) through the water for 10-sec intervals at different voltages at 25°. An almost identical curve was obtained at 180°.

The areas under the peaks obtained by passing nitrogen gas of flow rate 0.1 l/min through the tritiated water for different periods of time with a polarising potential of 72 V are shown by the broken line in Fig. 4. The areas were measured by cutting out the peaks from the recorder chart and weighing the paper. The variation of peak height shown by the continuous line were measured directly from the recorder chart. From this graph one can conclude that the area under the peaks is linearly related to the amount of tritium passing through the cell for vapours of constant activity. To test the variation of the area under the peaks with different specific activities, the tritiated water in T (Fig. 2) was diluted with known amounts of inactive water and the gas stream bypassed for 10-sec periods. Fixing the activity of the original water at the arbitrary value of 10, the results obtained are shown in Fig. 5. From Figs. 4 and 5 it is evident that there is a linear relationship between

the total activity passing through the cell and the area under the peaks at constant flow rate. The efficiency of the chamber, with a polarising potential of 72 V, was determined as 37 % by comparing the current obtained when the chamber contained a known amount of tritium (as water vapour) in nitrogen carrier gas with the value calculated from the equation given earlier.

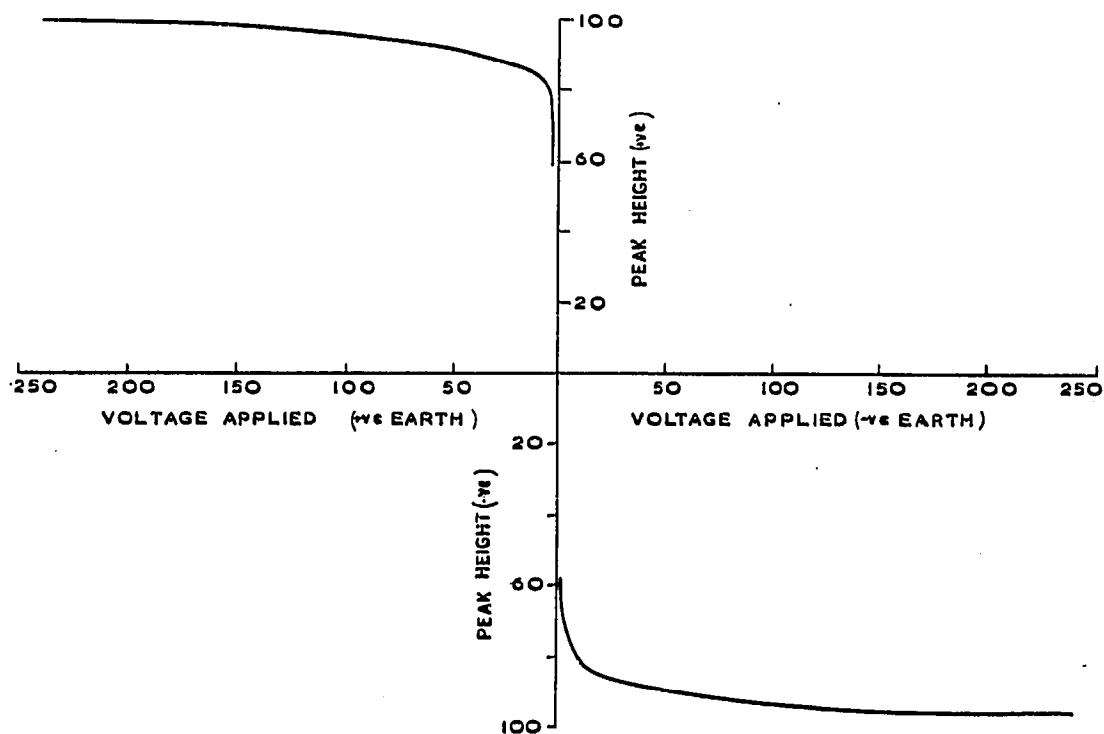


Fig. 3. The effect of variation of voltage on peak height.

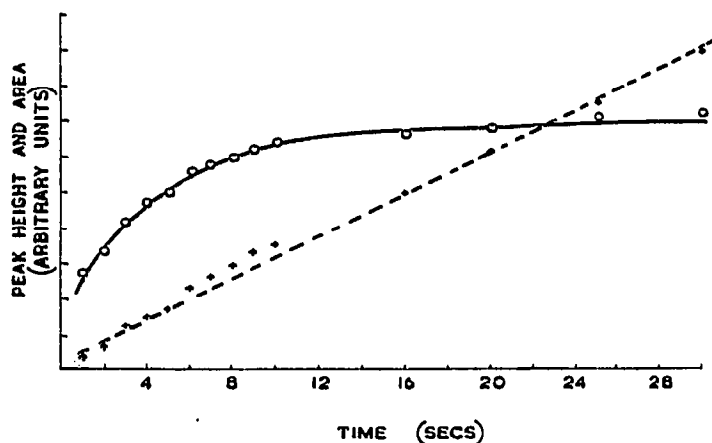


Fig. 4. The effect of bypassing the gas stream through tritiated water on peak height (continuous line) and area under the peaks (broken line) for different periods of time.

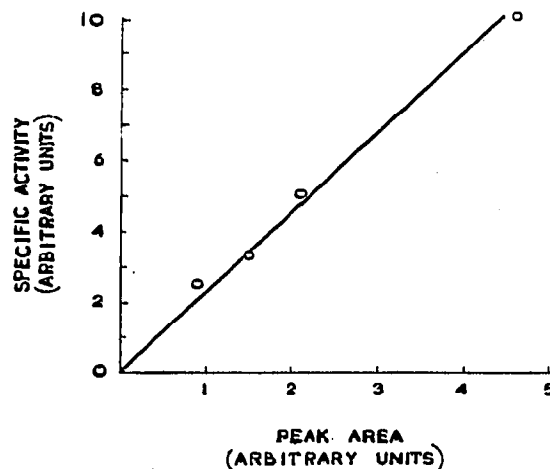


Fig. 5. The effect of bypassing the gas stream through water containing varied concentrations of T_2O before passing it through the ionisation chamber.

COMPARISON OF DETECTORS

Ionisation chambers are comparatively simple and robust detectors capable of measuring a very wide range of activities but are less sensitive than other methods. The one described in this paper has been used at temperatures up to 190°, and gives a good peak with about 0.5 μC of tritium; this sensitivity could probably be improved using a vibrating reed amplifier. The upper temperature limit at which it could be used was not determined; PTFE is chemically stable up to about 300° although other factors may prohibit its use at such high temperatures. Plastic scintillators are limited to use at room temperature; a design using a channelled inorganic scintillator and a suitable light guide could possibly be developed as a high temperature scintillation detector. The arrangement of CAMERON, BOYCE AND TAYLOR had a background count of 5 c.p.s. at 20° and the amount of activity needed to give a good peak (about 50 c.p.s.) at an efficiency of 2 % is about 0.07 μC of tritium. The methods of LOWE AND MOORE, and WOLFGANG should give a tenfold increase in efficiency on this but have drawbacks. The LOWE AND MOORE method gives an integrated record and it would be difficult to detect fractions containing a small amounts of activity if they were to follow a fraction of high activity. In the WOLFGANG method the position of the counting plateau varies with the proportion of methane in the counting mixture; it would therefore be necessary to exercise careful control over this factor, especially at high temperatures where the plateau length is reduced.

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SUMMARY

With the increase in the use of tritium as a radioactive tracer, several methods for measuring tritiated materials as they come off a vapour phase chromatography column have been developed. The author gives a very brief review of scintillation and proportional methods and a more detailed account of a gas flow ionisation chamber that has been used at temperatures up to 190°.

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