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# CONTINUOUS DETECTION OF RADIOACTIVE GAS CHROMATOGRAPHIC EFFLUENTS BY LIQUID SCINTILLATION

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## SUMMARY

A system for the detection of radioactive effluents from a gas chromatograph is described. The effluents are continuously dissolved in a stream of scintillator solution. After most of the carrier gas has been split off, the solution is led at a constant rate through a helical flow cell inserted in a liquid scintillation counter. The main advantages of the system are its expediency for all radioactive compounds, the absence of tailing or memory effects, good resolution and high sensitivity (less than 0.5 nCi). Peak fractions can be collected after they have passed through the flow cell for accurate activity measurements. The method is also suitable for distinguishing between compounds labelled with two different radioactive isotopes.

## INTRODUCTION

Methods for the detection of radioactive effluents from a gas chromatograph have been extensively reviewed by KARMAN[1]. As yet, no generally applicable method has been found.

Fractions can be collected in cooled traps, on solid supports or in solvents, and then subjected to homogeneous[2,3] or heterogeneous[1,2,4] scintillation counting, but these methods are neither direct nor continuous. Moreover, with high-boiling compounds there is a risk of premature condensation or aerosol formation, while volatile compounds may be incompletely absorbed on the solid support. Continuous integrated counting[2,5] can be applied to effluents trapped in a scintillation solution. The sensitivity, however, decreases as the number of radioactive materials dissolved increases, while the risk of premature condensation is still present. Condensation is also the major drawback when the effluent is continuously monitored with a proportional gas-flow counter[6]. Oxidation of the effluent before it is led through a proportional counter[7,8] diminishes the risk of contamination, but this approach is only applicable for $^{14}C$-active organic compounds that contain hydrogen and oxygen. Destructive hydrogenation[7,8] is the most widely applicable method of detection of radioactive effluents, as it excludes the possibility of gas quenching by halogens or nitrogen and sulphur oxides, and enables tritium-labelled compounds to be accurately monitored as well. A major disadvantage, however, is that not all radioactive materials are hydrogenated instantaneously. Moreover, adsorption on the catalyst sometimes

occurs, which results in peak tailing. The extent of the tailing increases as the catalyst becomes poisoned during use. Furthermore, minor disadvantages are that the radioactivity cannot be recovered once the materials have been passed through the counter, that $^{35}S$ activity cannot be assayed because sulphur-containing compounds become bound to the catalyst, and that $^{14}C$ and $^{3}H$ activities cannot be distinguished.

We have developed a system in which the effluents from a gas chromatograph are dissolved continuously in a stream of scintillator solution. A recently patented apparatus[9], designed for similar operations, was considered to have too large a mixing chamber, which reduces the resolution and increases the risk of premature condensation. In our system, premature condensation is prevented by maintaining the temperature of the gas stream at 250° until it actually reaches the liquid. The radioactivity of the resulting solution is subsequently assayed in a liquid scintillation flow cell.

## MATERIALS AND METHODS

The system is shown in Fig. 1. A Hewlett-Packard 5750 gas chromatograph, with an all-glass injection liner, column, splitter and effluent liner[10], is fitted with a specially designed detachable effluent liner extension, made of glass and Kovar metal (Fig. 2), through which the major part (90%) of the column effluent is led. The metal part of the effluent-liner extension, which is silanized before use, is maintained at 250° by means of an aluminium heating block. The effluent gas (flow-rate 18 ml/min) is brought into close contact with a stream of counting solution in a glass mixing tube fused to the liner exit. The counting solution (toluene containing 5 g/l of PPO and

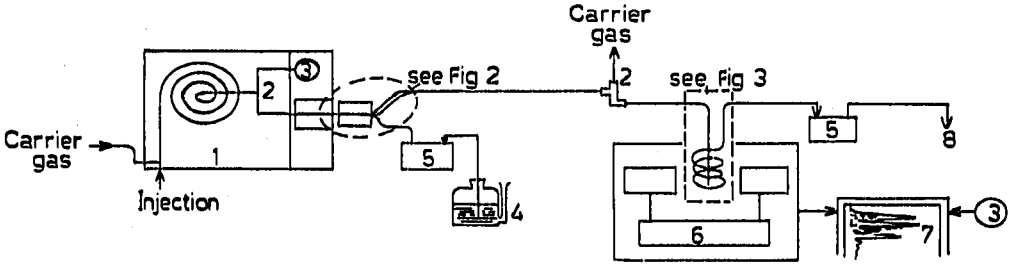


Fig. 1. Schematic representation of the continuous detection of radioactive gas chromatographic effluents. 1 = Gas chromatograph; 2 = splitter; 3 = flame ionization detector; 4 = container with scintillator solution; 5 = peristaltic pump; 6 = liquid scintillation spectrometer; 7 = two-pen recorder; 8 = fraction collector.

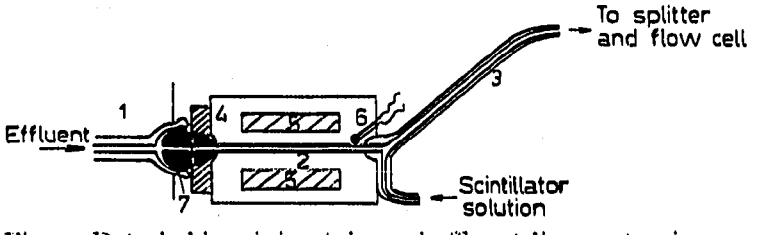


Fig. 2. Detachable mixing tube and effluent-liner extension. 1 = Gas chromatograph with glass effluent liner; 2 = narrow-bore (0.8 mm) liner extension of Kovar metal, fused to glass mixing tube and to stainless-steel ball-joint; 3 = glass mixing tube; 4 = aluminium heating block; 5 = heating elements (119 V each); 6 = iron–constantin thermocouple; 7 = O-ring.

0.3 g/l of POPOP) is introduced into the lower end of the mixing tube with a peristaltic pump (LKB 12000) at a flow-rate of 1.5 ml/min. All of the interconnecting tubing is made of toluene-resistant Acidflex (Technicon, Rotterdam). Just before the solution enters the liquid scintillation flow cell, the major part of the carrier gas is split off. The solution, together with a few gas bubbles to prevent mixing, is pumped by means of a second peristaltic pump (flow-rate 2 ml/min) through the helical flow cell (Fig. 3), which is made of borosilicate glass and has an effective volume of 1.4 ml. The liquid scintillation counter is a Tracerlab Coruflow Model SCE-542 with twin spectrometer and lin/log ratemeters. A two-pen recorder (Servogor 2, RE 520) is connected to the spectrometer and to the flame ionization detector of the gas chromatograph.

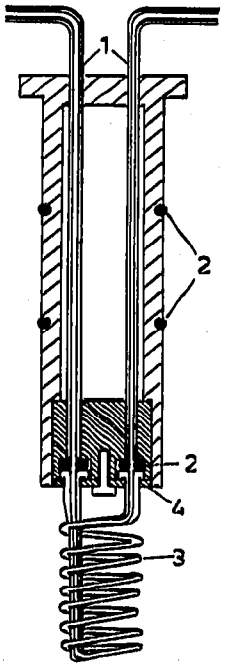


Fig. 3. Liquid scintillation flow cell with probe. 1 = Stainless-steel pipes; 2 = Viton rubber O-rings; 3 = interchangeable borosilicate glass cell; 4 = semi-circular collar discs to press the cell against the O-rings.

After it has passed through flow cell and pump, the scintillator solution can be collected in fractions and the total radioactivity of a peak fraction can be determined. This measurement is carried out in a Packard Tri-Carb Model 3380 liquid scintillation counter. The counting efficiency $E(\%)$ of the flow-cell is calculated from the equation

$$E = \frac{c}{d'} \cdot \frac{F}{V} \cdot 100$$

where $c$ is the integrated count after elution of the peak, $d'$ (disintegrations/min) is the absolute activity determined after collection, $F$ (ml/min) is the flow-rate of the second peristaltic pump and $V$ (ml) is the effective volume of the flow cell.

The radioactive materials for the first trial runs were [1,3-$^{14}$C]acetone, [1-$^{14}$C]-dodecanol-1, [1,2-$^{3}$H]hexadecane (all obtained from The Radiochemical Centre, Amersham, Great Britain), methyl [1-$^{14}$C]benzoate and pentyl [1-$^{14}$C]acetate (both prepared from Radiochemical Centre materials). The column of the gas chromatograph (2 m × 2 mm) was packed with 10 % Apiezon L and 1 % Carbowax on Diatoport S, 60–80 mesh. A run was also made with a $^{14}$C-labelled amino acid mixture (obtained from The Radiochemical Centre), diluted with inactive amino acids. The mixture was treated with ethanolic HCl and with trifluoroacetic anhydride[11,12]. A sample with an activity of 240 nCi was injected onto a 3 m × 2 mm column packed with 10% QF-1 on Diatoport S. In a further experiment, solutions of [4-$^{14}$C]cholesterol and [U-$^{3}$H]cholesterol in benzene were chromatographed in turn on a 1.5 m × 2 mm column with 3 % Silicone JXR on Gas-Chrom Q (100–200 mesh). The procedure was repeated with different amounts of the solutions.

## RESULTS

Fig. 4 shows the recorder response to the flame ionization detector (FID) and the scintillation flow detector (SFD) as a function of the elution time for the gas chromatographic separation of a mixture of $^{14}$C-labelled acetone, pentyl acetate, methyl benzoate and dodecanol in propanol. A correction has been made for the time interval between the signals from the two detectors (about 40 sec). The activities of acetone and pentyl acetate were each about 0.2 nCi. Even for such low levels of activity, the SFD signal could be clearly distinguished from the background.

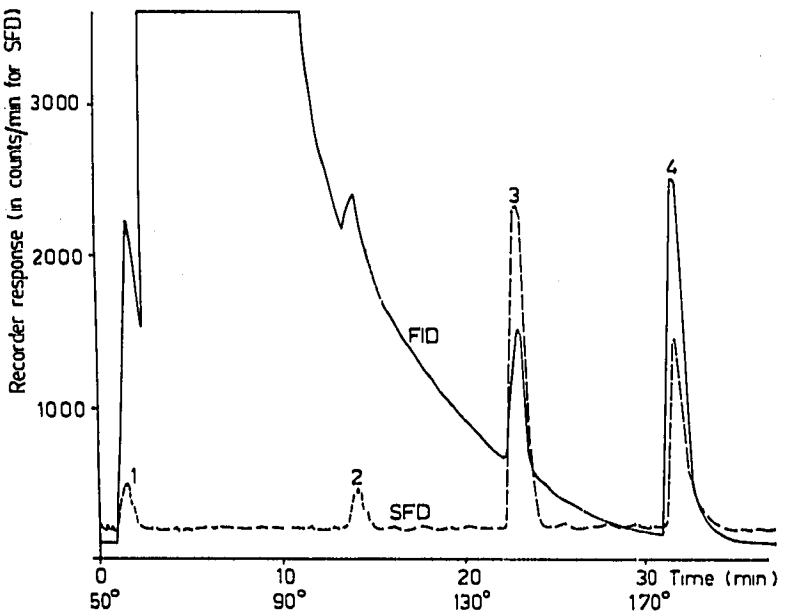


Fig. 4. Detection of $^{14}$C-labelled compounds. 1, Acetone (0.2 nCi); 2, pentyl acetate (0.2 nCi); 3, methyl benzoate (2 nCi); 4, dodecanol (1 nCi).

Fig. 5 shows the FID and SFD signals for two identical injections of methyl benzoate in propanol, separated by a 2-min interval. The good resolution of the system and the absence of significant peak broadening are evident.

A mixture of methyl [1-$^{14}$C]benzoate and [1,2-$^{3}$H]hexadecane in propanol was

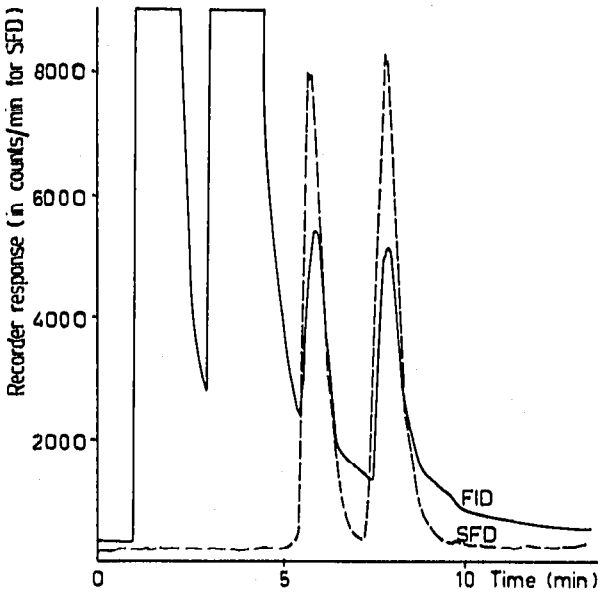


Fig. 5. Detection of two successive injections of $^{14}$C-labelled methyl benzoate (6 nCi). Oven temperature maintained at 150°.

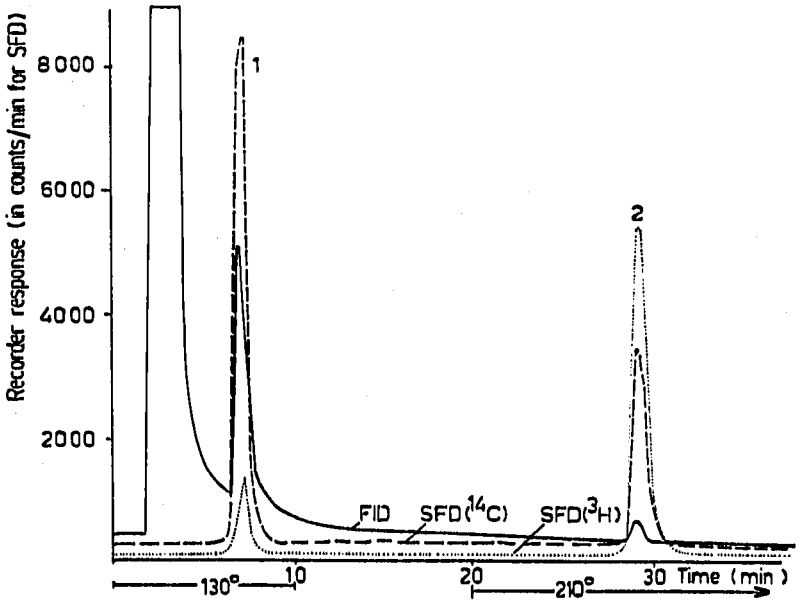


Fig. 6. Dual-channel detection of labelled compounds. 1, Methyl [1-$^{14}$C]benzoate (6 nCi); 2, [1,2-$^{3}$H]hexadecane (10 nCi).

separated and the activity of the effluent was measured in two different spectrometer channels (Fig. 6). The counting efficiency for $^{14}C$ was 85 % (in the $^{3}H$-channel, 17 %), and for $^{3}H$ 27 % (in the $^{14}C$-channel, 17 %). The background was 150 counts/min in the $^{14}C$-channel and 40 counts/min in the $^{3}H$-channel.

Fig. 7 shows the recorder response for the mixture of trifluoroacetylated ethyl esters of sixteen $^{14}C$-labelled amino acids. There was no evidence of peak broadening or tailing in the SFD signal. No effort was made to optimize the esterification of the amino acids or the gas chromatographic separation or to identify the inactive materials or the impurities with high specific activities.

The recorder response enables the specific activity of a labelled compound, expressed as the ratio between the SFD and FID peaks, to be calculated. This was carried out several times for both the $^{14}C$-labelled and $^{3}H$-labelled cholesterol. For each of these compounds, the variation in the calculated specific activity was less than 2 %.

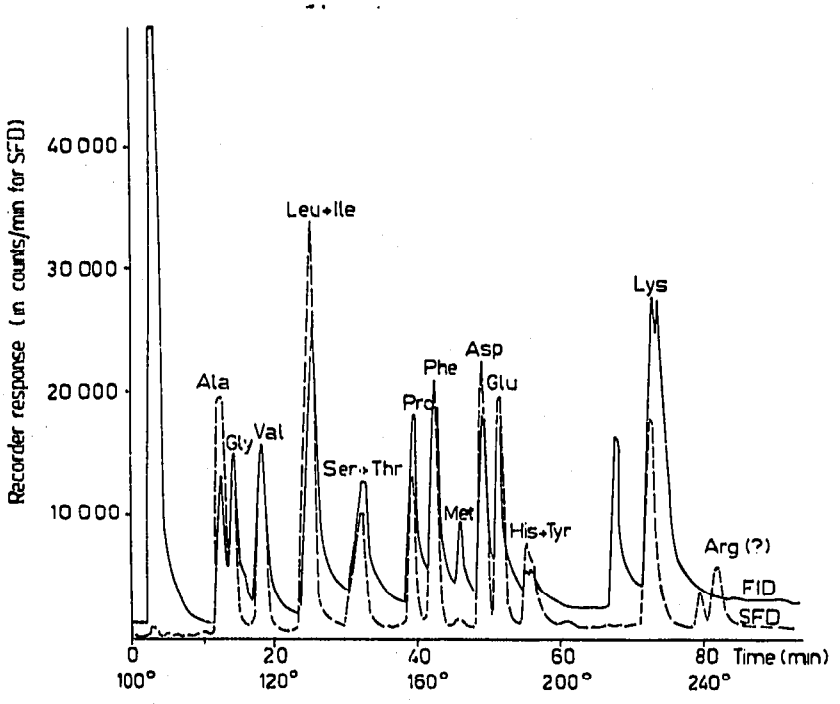


Fig. 7. Detection of trifluoroacetylated ethyl esters of sixteen $^{14}C$-labelled amino acids.

## CONCLUSIONS

The system described facilitates the reliable detection of radioactive compounds in a vapour stream, particularly in the effluent of a gas chromatograph. Even compounds with a very high vapour pressure, such as cholesterol or amino acid derivatives, were monitored with no loss of resolution. As the contact between the vapour and the scintillator solution lasts for several seconds, hardly any material is lost as a result of aerosol formation. Even at very high temperatures of the trapping tube (up

to 290°), this loss was not more than a few per cent. A plume of aerosol, which apparently originated from the toluene in the scintillator solution, was sometimes observed at the gas exit, and was prevented by local heating of the exit pipe with a small thermo-element at about 80°.

The main advantages of the system can be summarized as follows:

(1) Detection is efficient and the resolution equals that of the FID signal.

(2) Compounds are monitored directly without the need for catalytic destruction.

(3) $^{14}C$- and $^{3}H$-labels can be distinguished with the aid of two spectrometer channels.

(4) After detection, the compounds can be collected in scintillation vials for accurate counting.

## COMBINATION OF DETECTION SYSTEMS FOR GAS AND LIQUID CHROMATOGRAPHY

A major drawback to the method is that a liquid scintillation counter is expensive for use as a gas chromatographic detector. Such an instrument, however, may have other applications; it can, for instance, be used for the continuous monitoring of radioactive effluents in liquid–liquid chromatography, as described in a previous paper[13]. The monitoring systems for both gaseous and liquid radioactive effluents can conveniently be combined in an apparatus of the type shown in Fig. 8. The circuit for the monitoring of gas chromatographic effluents is represented by continuous lines, while the broken lines show the circuit for liquid chromatography. The choice of system is determined by the three selection switches, which are simply clamps on the Acidflex tubing. The pump for both systems is a Cenco twelve-channel model.

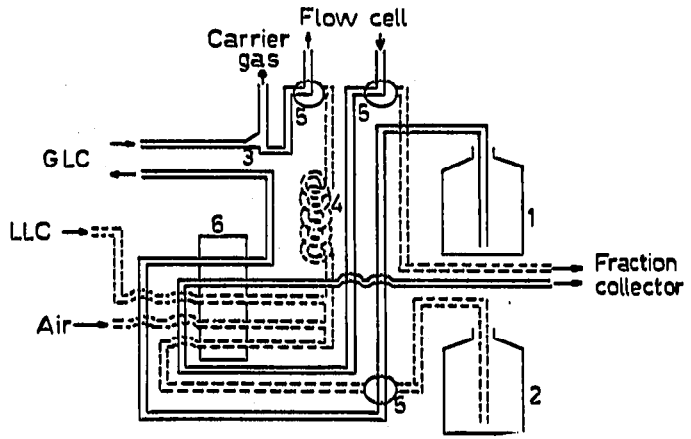


Fig. 8. Combination of monitoring systems for gas chromatography (continuous lines) and liquid chromatography (broken lines). 1 = Scintillator solution for gas chromatography; 2 = scintillator solution for liquid chromatography; 3 = gas–liquid splitter; 4 = mixing spiral; 5 = selection switches; 6 = pump.

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