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SCINTILLATION COUNTER FOR CONTINUOUS MONITORING OF RADIOACTIVITY IN SOLUTIONS

K. H. CLIFFORD, A. J. W. HEWETT AND G. POPJÁK*

"Shell" Research Limited, Milstead Laboratory of Chemical Enzymology, Broad Oak Road, Sittingbourne, Kent (Great Britain)

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SUMMARY

A scintillation counter, suitable for the measurement of radioactivity in solutions irrespective of the nature of the solvent, is described. The instrument has been developed specifically for the continuous monitoring of effluents from chromatographic columns. Beads of a lithium-cerium glass, insoluble in all solvents except hydrofluoric acid, in a shallow flow-cell act as scintillator; the photons are detected with a pair of photomultipliers with coincidence circuit in conjunction with a rate-meter. The efficiency of counting ^{14}C and ^{35}S in solution is better than 20%; for ^{32}P the efficiency is about 90%, for ^{36}Cl 63%, but for ^3H it is only 0.3%, depending on photomultiplier and discriminator voltages and temperature selected.

INTRODUCTION

Several instruments have been described for the monitoring of radioactive isotopes by scintillation counting in effluents from column chromatography¹⁻⁴, but their use is limited to a few solvent systems because the scintillators employed are attacked by other solvents. For example, anthracene is suitable only with aqueous systems; even the use of plastic scintillators is restricted.

We have tested a lithium-cerium glass scintillator, NE 901, (Nuclear Enterprises (G.B.) Ltd.), which is insoluble in all solvents except hydrofluoric acid, and found it to respond well to ^{14}C in solution and that it could be used for the detection of ^3H -labelled compounds of high activity and of other isotopes. Its only disadvantage seems to be that, because of its strong phosphorescence after exposure to light, the counting cell filled with scintillator beads has to be kept in the dark for 24-48 h before a steady background counting rate can be obtained from it.

A europium-activated calcium fluoride powder gave a higher efficiency for ^{14}C than the glass scintillator and showed no phosphorescence; however, it is appreciably soluble in ammonia.

The monitor we have developed consists of a borosilicate glass optical cell 1 mm

* Present address: Department of Biological Chemistry, University of California, Los Angeles, and Center for the Health Sciences, Los Angeles, Calif. 90024, U.S.A.

deep, filled with 250–300 μ diameter beads of the glass scintillator, placed between two photomultiplier tubes, in conjunction with a rate-meter suitable for coincidence counting. The output of the rate-meter is fed into a 100 mV recorder.

CONSTRUCTION OF INSTRUMENT

Photomultiplier housing and cell holder

Fig. 1 shows the individual components of the counter. Various stages of assembly are shown in Figs. 2 and 3. The two photomultiplier tubes (type 9634 QA; selected pair; E.M.I. Ltd.) are housed in a plastic pipe impervious to light (16 in. long, 2 in. I.D., Fig. 1A) with a 1/4 in. slot cut out at its middle to a depth of one-half of its diameter (Fig. 1B). The photomultipliers are pushed into the tube and are held

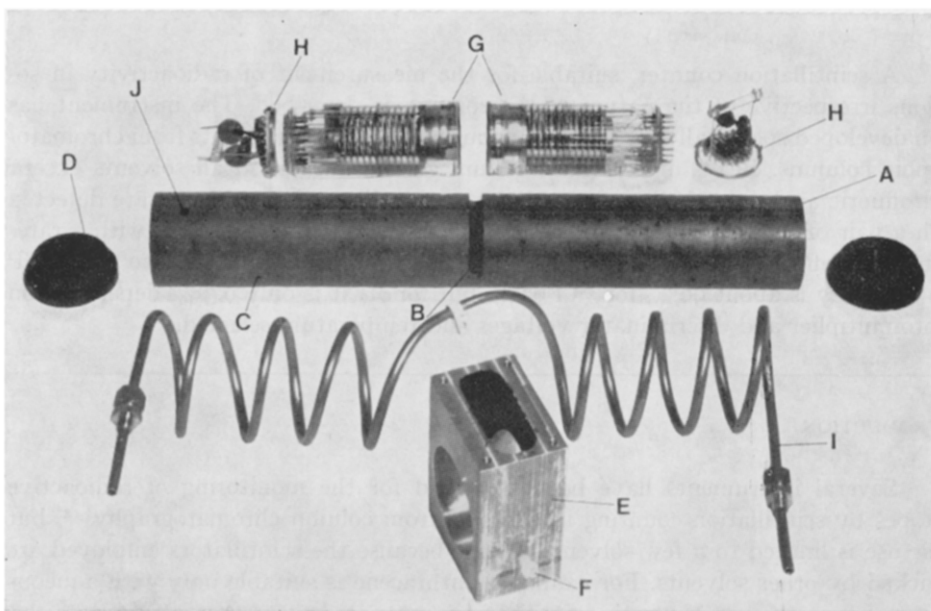


Fig. 1. Components of photomultiplier assembly: (A) Photomultiplier housing; (B) slot for counting cell; (C) tapped hole for nylon screw securing photomultiplier base; (D) plastic end-caps; (E) cell-housing; (F) nylon screw securing cell-holder to photomultiplier housing; (G) photomultiplier tubes; (H) photomultiplier connecting base; (I) cooling coil; (J) cable inlet.

in position with nylon screws tapped through the wall of the plastic holder so that their windows are level with the edge of the slot. The nylon screws locate through the fixing holes in the lugs of the photomultiplier connecting base, the lugs having been bent at right angles (Fig. 1C). The photomultiplier housing, including two recessed black plastic end-caps (Fig. 1D), is 16.7/8 in. long.

The cell-holder is made out of an aluminium block, 3 \times 2 \times 4 in. A hole is cut through the 3 \times 4 in. faces to allow a snug fitting of the tube bearing the photomultipliers. A cavity 2.1/2 \times 1 in. and 2.1/4 in. deep is then milled out of the block from one of its 3 \times 2 in. faces (Fig. 1E). The cell-holder is pushed over the photomultiplier housing until the slot in the tube comes to the middle of the cavity of the

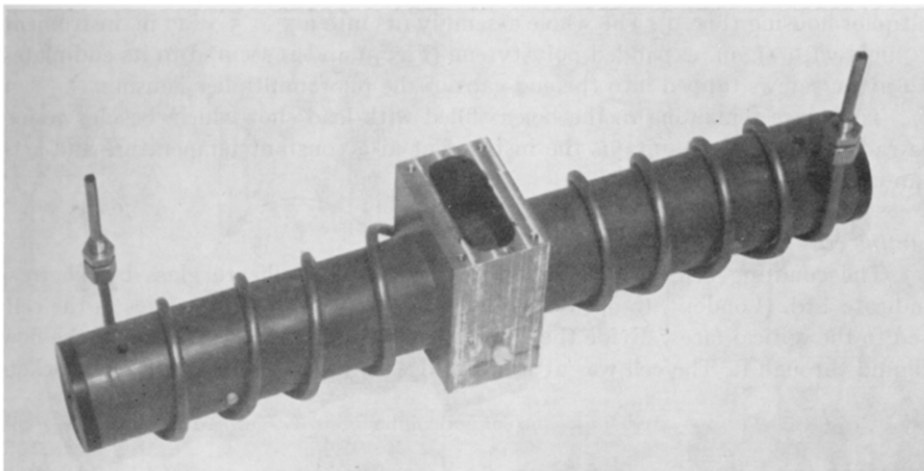


Fig. 2. Assembly of photomultiplier housing and cell-holder.

cell-holder (Fig. 2) and is secured to the photomultiplier housing by a nylon screw tapped through the cell-holder (Fig. 1F). The cell-holder is covered with a 1/2 in. recessed lid secured to the cell-holder with four screws. Two holes are drilled at an angle through the lid at one side for the connecting tubes to the counting cell (Figs. 3 and 4). A cooling coil, made of 1/4 in. O.D. copper pipe, is wound around the photo-

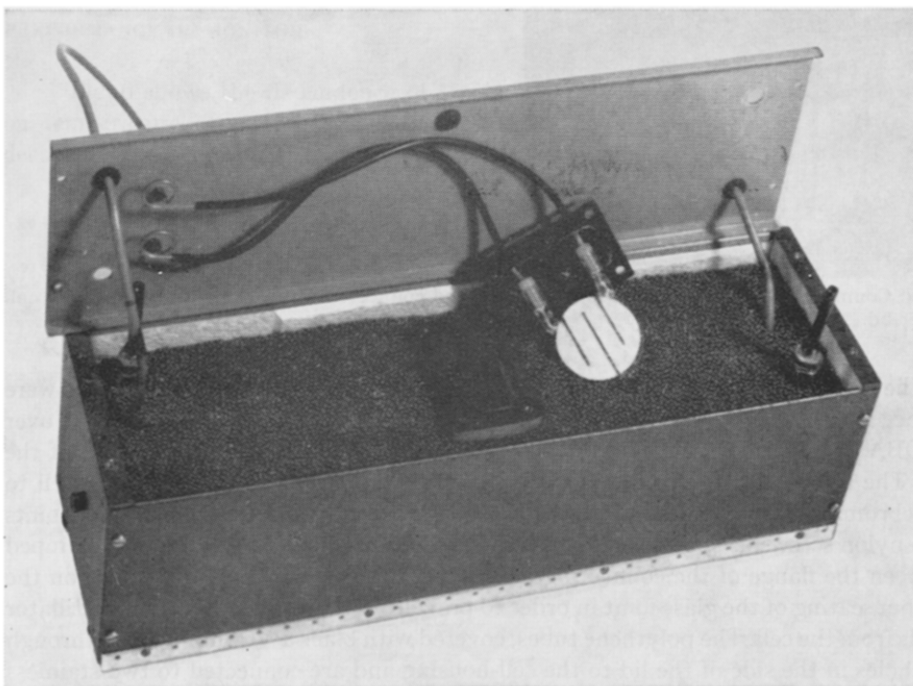


Fig. 3. Complete instrument showing counting cell in position in lid of cell-holder.

multiplier housing (Fig. 2). The whole assembly fits into a $5 \times 5 \times 17$ in. instrument box lined with $1/2$ in. expanded polystyrene (Fig. 3) and is secured to its end-plates with nylon screws tapped into the end-caps of the photomultiplier housing.

The space remaining in the box is filled with lead shot which, besides acting as a radiation shield, maintains the instrument at a constant temperature and acts as an effective light-trap.

Counting cell

The counting cell, 1 mm deep, was made of borosilicate glass by Thermal Syndicate Ltd. (London), to our design (Figs. 4 and 5). The baffle plates in the cell, fused to the optical faces, divide the cell into four compartments and direct the flow of liquid through it. The cell was at first fitted with C5 standard taper glass sockets

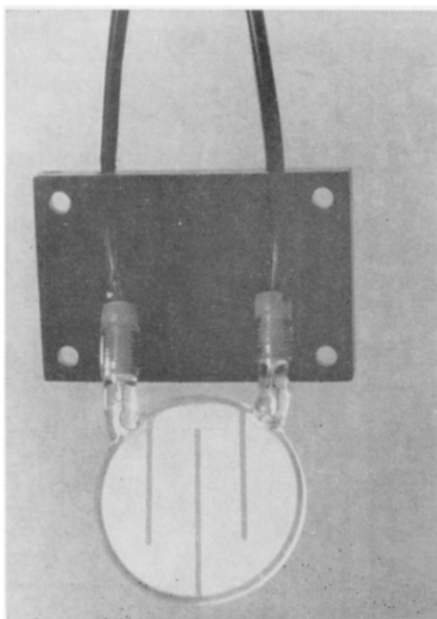


Fig. 4. Counting cell filled with scintillator beads and connected to polythene tubes through cell holder lid.

for the inlet and outlet connections; these, however, proved troublesome and were replaced with threaded glass joints. These threaded glass joints were formed over an OBA brass studding and were then fused onto the inlet and outlet ports of the cell. The locking of the flanged polythene tubes (3 mm O.D.) connecting the cell to the chromatographic column and fraction collector, into the threaded glass joints with nylon screws, is shown in detail in Fig. 5. A platinum filter (80 mesh) is clamped between the flange of the connecting polythene tube and a polythene washer on the bottom seating of the glass joint in order to prevent the washing out of the scintillator beads from the cell. The polythene tubes, covered with black PVC tubing, pass through two holes in the side of the lid to the cell-housing and are connected to two stainless steel tubes fitted onto the lid of the instrument box (Figs. 3 and 4).

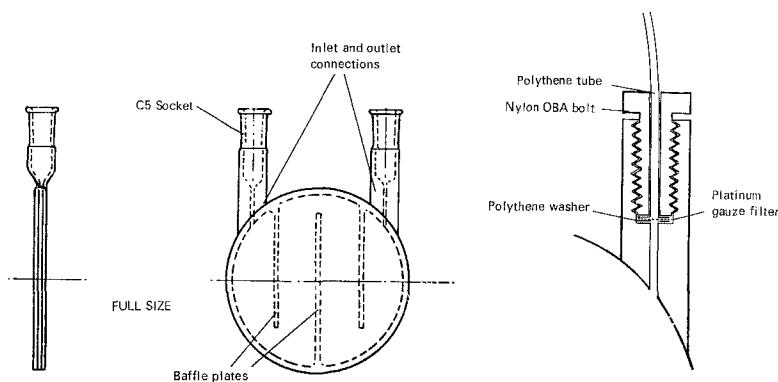


Fig. 5. Diagram of counting cell and modification to connecting ports (scales: left, 1:2; right, 1:1).

The cell is filled with the glass scintillator powder, NE 901, 250–300 μ diameter, by sucking a suspension of the powder in water through one of the ports before the platinum filter is fitted into position. The stream of water sucked through the cell carries the powder from one compartment to the other until the cell is completely filled. The powder is finally packed by drawing ethanol or methanol through the cell. After filling the cell, the wire filter is clamped into position, the cell is placed into the cell-housing, the connecting tubes are drawn through the lid of the housing and the lid is secured into position.

PERFORMANCE OF MONITOR

Fig. 6 shows the dependence of the background counting rate of the monitor on temperature after the light-induced α -phosphorescence of the scintillator has decayed. Since the radiation-induced β -phosphorescence of the scintillator is inde-

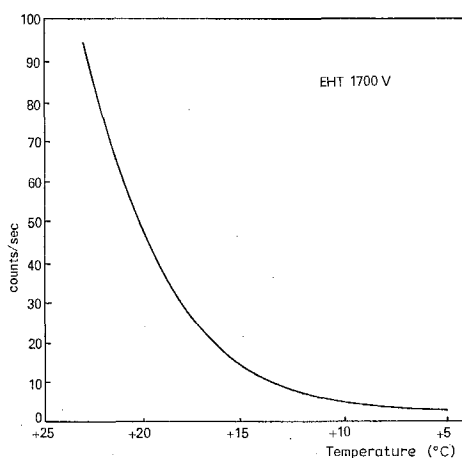


Fig. 6. Background counting rate including scintillator as a function of temperature at fixed photomultiplier and discriminator voltages (1700 and 5 V, respectively).

TABLE I

BACKGROUND COUNTING RATES (IN COUNTS PER SECOND) AT $+5^{\circ}$ AND AT VARIOUS PHOTOMULTIPLIER AND DISCRIMINATOR BIAS VOLTAGES

Bias (V)	Photomultiplier		
	1800 V	1700 V	1600 V
5	3.0	2.5	2.8
10	2.7	2.3	2.5
15	2.4	2.0	1.8
20	2.2	1.7	1.5
35	1.7	1.2	1.2
50	1.2	1.0	0.8

pendent of temperature, the efficiency of isotope counting is unaffected by cooling. The background counting rate at various photomultiplier and bias voltages at $+5^{\circ}$ of the tubes is shown in Table I.

The efficiency of counting ^{14}C , using a standard [^{14}C]toluene in the cell, with various bias voltages at set photomultiplier voltages is shown in Fig. 7. From the graph it can be seen that at 5° , and 1700 V, with 5 V bias, the efficiency of the monitor for ^{14}C is 21%. If, however, cooling the column effluent is unacceptable, a

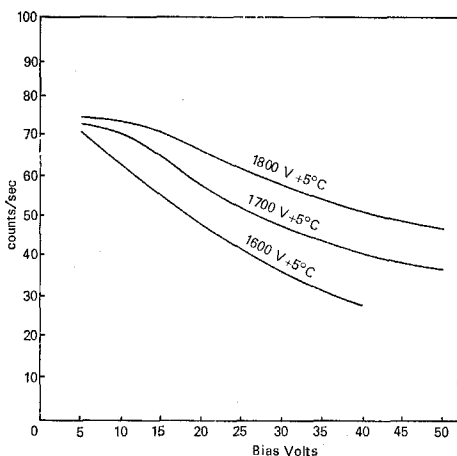


Fig. 7. Counting rates less background counts with a [^{14}C]toluene ($700 \text{ disintegrations} \cdot \text{sec}^{-1} \cdot \text{ml}^{-1}$) cell volume of 0.5 ml as a function of photomultiplier voltage and discriminator bias voltage.

lower photomultiplier voltage has to be selected in order to reduce background counts at the expense of a lower efficiency of counting. A comparison of efficiencies for [^{14}C]toluene and [^3H]toluene at different temperatures, with scintillator beads of varying diameters, is shown in Table II.

The NE 901 scintillator, $250\text{--}300 \mu$ diameter beads, at room temperature and with 1100 V applied to the photomultipliers at 5 V bias, gave for various isotopes the efficiencies shown in Table III.

TABLE II

COUNTING EFFICIENCIES OF VARIOUS SCINTILLATOR BEADS WITH 1700 V APPLIED TO PHOTOMULTIPLIERS AND 5 V BIAS

Scintillator	Temperature (°C)	Diameter of scintillator beads (μ)	Counting efficiency	
			(%)	Isotope
NE 901	5	250-300	21	^{14}C
NE 901	5	125-150	30	^{14}C
NE 901	5	250-300	0.3	^3H
NE 901	5	125-150	0.4	^3H
CaF ₂ (Eu)	20 \pm 2	250-300	50	^{14}C

^{125}I has been used with this monitor for column effluents but as a standardized solution was not available we were unable to calibrate the monitor for this isotope. However, a high efficiency (approximately 60%) was obtained for uncalibrated materials.

Counting [^{14}C]carbon dioxide

The cell was tested for counting ^{14}C as carbon dioxide by pumping the gas through the cell in a closed circuit. Although the scintillator gave 90-100% efficiency for $^{14}\text{CO}_2$, the system is not practical for CO_2 counting at high gas-flow rates because the cell, after filling with the scintillator beads, has a gas volume of only about 0.7 ml.

TABLE III

COUNTING EFFICIENCY OF THE NE 901 SCINTILLATOR BEADS (250-300 μ DIAMETER) AT 20 \pm 2° WITH 1100 V APPLIED TO PHOTOMULTIPLIERS AND 5 V BIAS

Isotope	Counting efficiency (%)
^{14}C	10
^{32}P	92.5
^{35}S	10.5
^{36}Cl	62.5

USE OF THE INSTRUMENT

In practice we have been using the monitor in conjunction with chromatographic fraction collectors. The column effluent is led directly through the counting cell and then the effluent from the latter is taken to a fraction collector. The change of each collector tube is marked on the record of radioactivity, hence it is easy to identify fractions containing the isotopes. A typical record is shown in Fig. 8.

We have noted during two years use only one serious anomaly: strongly fluorescent substances (*e.g.* carotenoids) when chromatographed in light give high counting rates even though they may not contain any radioactivity. Spurious counts due to fluorescence are readily detected by the rapid decay of counts after stopping the

flow from the chromatographic column for a few seconds. Of course, radioactive fluorescent compounds can be monitored for radioactivity satisfactorily if the instrument is set up in a dark room, or if the chromatographic column and the plastic tube leading from the column to the monitor are shielded from light, *e.g.* by an envelope of black photographic paper.

“Memory” effects have been observed only with ^{125}I . When a mixture of ^{125}I -

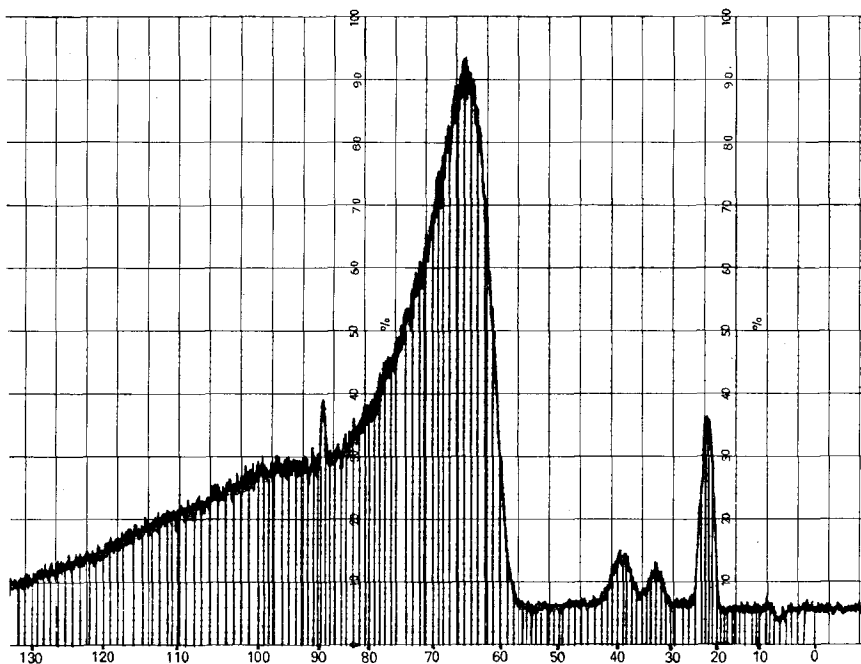


Fig. 8. Typical record obtained with instrument. This shows the separation of five fractions (^{14}C -labelled) from an incubation of yeast microsomes with farnesyl pyrophosphate (^{14}C -labelled). Chromatography of “compound X” prepared from [^{14}C]-FPP and yeast microsomes on Cellex D with 80 mM ammonium formate in methanol with a 0–300 mM NH_3 linear gradient. Counting rate: 0–100 c.p.s.; time constant: 20 sec; chart speed: 30 mm/h.

labelled iodohydrins containing a little elemental ^{125}I were chromatographed on a silicic acid column with benzene as the first solvent, the radioactive iodine was eluted with the solvent front and almost all of this remained adsorbed on the scintillator beads in the counting cell. Neither benzene nor subsequent changes of solvent to ethyl acetate–benzene mixtures shifted the iodine from the scintillator. The iodine nevertheless could be washed out very easily with methanol. The ^{125}I -labelled iodohydrins, on the other hand, were not adsorbed onto the scintillator.

In spite of these few shortcomings, the counting system described has found wide application in our laboratory mostly for detecting ^{14}C in effluents from column chromatography. It has been used with solvents such as water, ammonia, methanol, ethanol, isopropanol, ethyl acetate, hexane, benzene, chloroform, and ether.

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