

DETERMINATION OF WEAK BETA EMITTERS BY LIQUID SCINTILLATION COUNTING TECHNIQS

III. INVESTIGATION OF ORGANIC CRYSTAL AND PLASTIC FLOW CHAMBER DETECTORS

By

G. TÖRÖK, G. PARLAGH and L. G. NAGY

Department of Physical Chemistry, Technical University, Budapest

(Received September 16, 1968)

Presented by Prof. Dr. G. VARSÁNYI

1. Introduction

In our earlier investigations, problems of measuring techniques concerning C—14 and S—35 liquid scintillation counting were discussed [1], and the possibilities of measuring gaseous samples in the liquid phase were studied [2]. The conclusion was drawn that this type of measuring was tiresome, exacting with respect to equipment, and moreover, the reproducibility was unsatisfactory. Difficulties arose also from the fact that the sample to be measured and the scintillator form a common system, and this necessitates a strictly defined sample preparation and composition.

Owing to the above reasons, the possibility of a direct, preferably continuous measurement in the gaseous and liquid phases was investigated.

It was endeavoured therefore to develop a measuring method for heterogeneous phase systems, in which the "preparatory operations" could be eliminated, i.e. direct measurement could become possible.

We wish to mention that weak beta counting with heterogeneous phase liquid scintillators is not discussed, in general, among liquid scintillation counting techniques in the strict sense. Nevertheless, identical principles valid and the common measuring problem make a joint discussion likely to be advantageous.

2. Survey of the literature

Heterogeneous phase scintillation counting techniques for the detection of weak beta emission, reported in the literature, can be classified into three groups:

1. measuring in suspensions and gels,
2. measuring on filter paper, and
3. measuring with plastic and disperse phosphors.

Ad 1. Measuring in suspensions of substances of poor solubility was recommended by HAYES [3].

The advantage of this method is the absence of chemical inhibition, and that the sample can be recovered by filtration; it has, however, the disadvantage that self-absorption occurs, and measuring is tiresome.

The time required increases because either repeated measurements are necessary in the intervals of which the sample must be shaken, or measurement must be continuous in time, and the counts must be extrapolated for zero time.

The suspended particles absorb part of the emitted light, but at the same time they act as reflectors. With the so-called white suspensions, the efficiency depends only very slightly on the concentration, but with coloured samples light absorption is considerable. The efficiency measured by homogeneous internal standard is about 60 per cent for C—14 and 20 per cent for H—3.

To stabilize the suspension and, consequently, to reduce time requirement, gelling agents are used. The best known among these is Cab-O-Sil (a finely dispersed SiO_2); upon adding 4% of Cab-O-Sil, a thixotropic gel, easy to handle, is obtained [4].

Ad 2. ROUCAYROL [5] was the first to show that when filter paper bearing an active sample was impregnated with a scintillator, the activity could be measured at good efficiency.

Instead of volatile toluene FUNT [6] recommended monoisopropyl-biphenyl as solvent.

Several variants of this measuring technique are known.

a) The filter paper strip impregnated with the scintillator is measured directly; with harder β -emitters, additional strips are necessary for the absorption of higher energy particles.

b) Anthracene microcrystals are formed in the filter paper strip.

c) The filter paper is measured in a vial filled with the scintillator. Thus, chromatograms can be continuously measured. For the determination of the efficiency it is, however, important to see if the sample is not eluted from the paper.

d) In the evaluation of radiochromatograms, the light emitted by the paper impregnated with scintillator can be recorded on an X-ray film. According to WILSON, at an exposition of 50 hours, an activity of $0.1 \mu\text{C}/\text{cm}^2$ can be detected [7]. PINTÉR [8] applies samples on a glass wool texture impregnated with silica gel. Discs are cut out (12 mm diameter), placed into a cell, and measured with 15 ml of scintillator. The efficiency is not affected by a possible elution of the sample. WEG [9] impregnates biological tissue preparations with the active substance, cut after drying into small pieces, and filled into the cell. For C—14 the efficiency is 39 per cent.

Ad 3. The application of the flow chamber detector made of a plastic phosphor was described first by SCHRAM [7]. The method has the advantage that no decontamination is needed, a constant geometry can be ensured, and high activities can be measured at a low background.

FUNT [10] used a helically wound plastic phosphorus capillary. The detector volume was 0.76 ml. Optical coupling between the capillary and the photomultiplier was provided by silicone oil. For C—14 the efficiency in the liquid phase was 5.7%, and in the form of $^{14}\text{CO}_2$ in gaseous phase 58%.

A similar apparatus is used by KIMBEL [11] for the continuous measurement of C—14 and S—35 in liquid phase. For C—14 (3 m μ C benzoic acid) the efficiency is 3%, for S—35 (66 m μ C $\text{Na}_2\text{S}_2\text{O}_3$) 1.3%.

Measurement in the heterogeneous phase can be done also with suspended phosphors, in form of plastic filaments or clumps, microcrystalline or pulverized organic phosphors, e.g. anthracene, PPO etc. Though the crystalline powder is not transparent, in a layer of the thickness required for absorption, the loss in light is not considerable.

STEINBERG added to a constant quantity of anthracene powder an always identical volume of the aqueous sample, and used a detergent to ensure efficient wetting [7]. The counting efficiency was 20% for C—14 and 0.5 per cent for H—3.

On the basis of these findings, SCHRAM [7] filled a polyethylene spiral with pulverized anthracene and, similarly as before, used silicone oil for optical coupling to the photomultiplier. This cell can be used both to discontinuous and continuous measurements. Moreover, it has the advantage of good reproducibility, and no sedimentation. Flow resistance and efficiency are dependent on the size of the crystal. In the measurement of C—14, dimension of 300 μ at 55 per cent efficiency can be accepted as an optimum.

3. Selection of the detector type

It will be clear from this brief survey that a flow counter made of a plastic or disperse phosphor is best suited for our problem.

Taking into consideration that in gaseous phase the highest efficiency is reported in the literature for the plastic scintillator capillary spiral, and in liquid phase for the anthracene powder chamber, it was decided to test these two types.

At the same time it had to be determined:

a) whether the detector, similarly to the scintillator solution, is attacked by free sulfur dioxide;

b) whether the sensibility stated can be ensured with the available substances;

c) which are the flow characteristics of the system, and whether it is suitable for the distortion-free indication of rapid activity changes;

d) whether the photomultipliers and electronics of the not specially low noise level, scintillation detectors of type ND—114 of normal design can be used for this purpose.

4. Anthracene powder detector

According to Schram, the anthracene powder used as scintillator — a non-fractionated commercial product of Packard — was filled into a polyethylene capillary. The tube of about 1 m length and 1 mm internal diameter was filled up to a height of 80 cm with the anthracene powder. The packing was sealed at the two ends by glass wool plugs.

This tube was wound into a spiral of 60 mm diameter and placed on the photocathode so that its surface was almost completely covered by the windings. Since the weight of the filled-in anthracene was 440.6 mg, the useful detector volume out of the total volume of 0.58 ml was estimated to be about 0.24 ml.

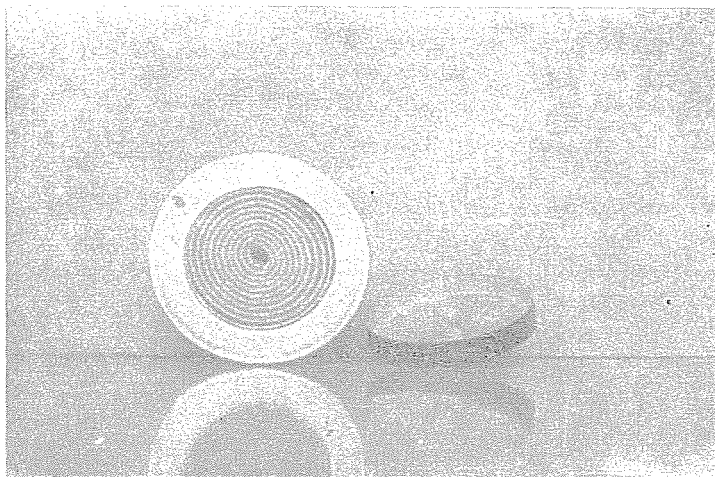


Fig. 1

Obviously, the exact detector volume cannot be determined in this way. Pertinent investigations will be discussed in the following.

A small detector volume is necessary to eliminate losses by self-absorption, and moreover, is advantageous in the measurement of small liquid samples or of rapid changes in activity.

When assembling the detector chamber, particular care must be taken to ensure its light-tight sealing. For this purpose, the spiral was placed into an aluminium block fitted to the photomultiplier, instead of the crystal.

Our experiments showed that the polyethylene tube was light-conducting. Therefore, a stainless steel extension tube of 20 mm length was fitted to both the inlet and the outlet of the polyethylene tube. Notwithstanding this arrangement, when the conduits contained a liquid, a shift of about 100 volts was observed on the background curves. Owing to this, external conduits had to be screened over a length of minimum 90 cm against light.

The photograph of the assembled detector is shown at the left side of Fig. 1. In view of the data reported in the literature, we intended to use this

detector exclusively for the measurement of liquid samples. A feeding system was constructed, which made continuous and discontinuous measurements possible. The schematic diagram of this feeder is shown in Fig. 2.

Flow conditions could be unambiguously fixed by means of gaseous nitrogen, the pressure of which was stabilized by a manostat, further by the height of the liquid in the microburette. The flow rate was determined from volumetric data read off the microburette, and from the volumetric or gravimetric measurement of the liquid collected in the receiver, arranged at the end

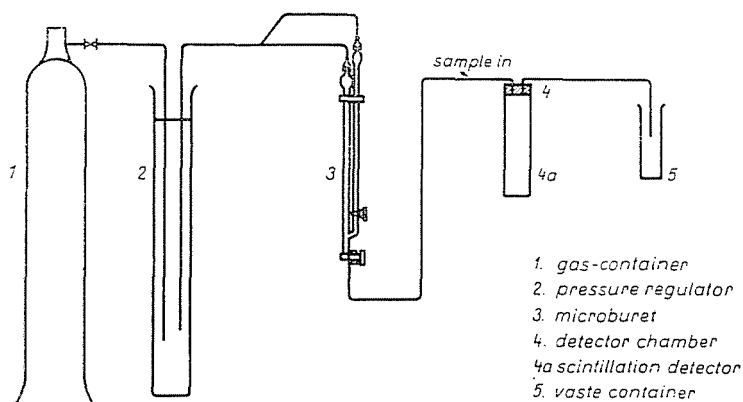


Fig. 2

of the system. In discontinuous experiments, the samples (of a volume of 1—500 μ l) were injected with a Hamilton syringe at the place marked by an arrow.

When choosing an appropriate flow rate, the measurement of a sample required only a few minutes.

A scaler, or a ratemeter combined with a recorder could be connected to the detector, so that measurements could be either discontinuous or continuous.

Before assembling the instrument, the dark noise, and after assembly the background was measured at various settings, to distinguish between pure background pulses and dark noise, and to determine maximum operational voltage. (The unjustified increase of background after filling up with water indicated the necessity of further light screening.)

As the next step of setting, the whole detector was filled with S—35 labelled Na_2SO_4 solution, and the characteristics were plotted (Fig. 3). Efficiencies were calculated on the basis of the useful volume, determined as discussed in the following.

It has been established that

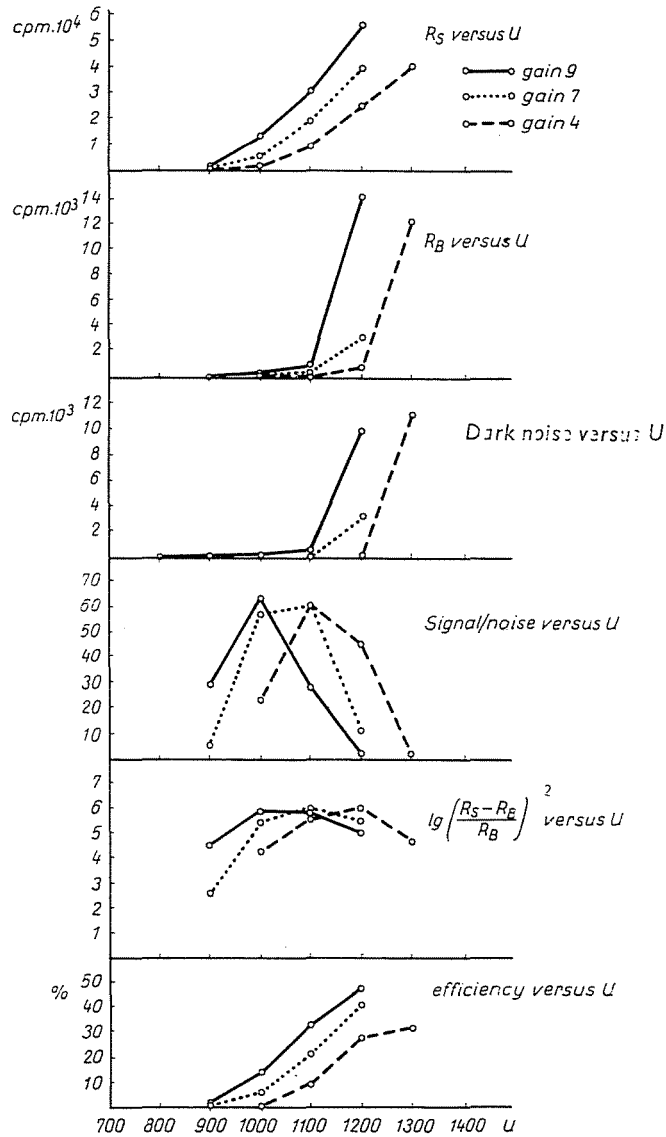


Fig. 3

a) though the maximum high voltage was limited by the high dark noise of the photomultiplier to 1200 V, an efficiency of 40 per cent could be measured at an acceptable signal/noise ratio.

b) at an optimum signal/noise ratio or rather $\lg \frac{(R_s - R_b)^2}{R_b}$ value (where R_s = the signal and R_b the background), the efficiency for S-35 beta radiation was 20 to 30 per cent.

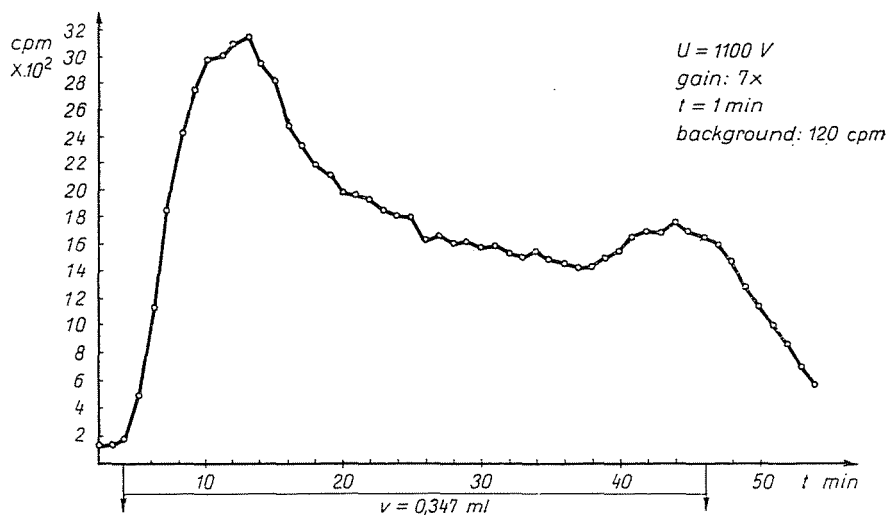


Fig. 4

c) these data could be improved with a low-noise photomultiplier or by cooling the photomultiplier.

d) the activity of soft beta emitter isotopes, thus of S—35 and C—14 could be measured with this detector without the use of any special auxiliary equipment. According to our experiences, the spiral can quickly be decontaminated. After removing the active solution, and after passing water (a few times the detector volume) through the detector, the background was diminished to its original value.

Data determined by the diameter of the tube, its length, and by the volume of the anthracene powder could not be accepted as the reliable useful dimensions of the detector. This value, on the one hand, comprised also a dead volume and, on the other hand, it could have changed during the preparation, shaping, and pressure testing (1.5 atm) of the detector.

Owing to these reasons, the required volume was determined as follows:

A small volume of the active liquid sample as compared to the volume of the detector, in our case 1—10 μl , was fed into the flowing "carrier liquid" (water). It was assumed, and has been verified, that at a moderate flow rate (0.5 ml/hour) the active "liquid plug" introduced did not mix with the carrier liquid, but passed through the column keeping sharp fronts. At the same time, it was to be expected that the "rate of the running up" of the intensity would be greater than its "rate of running down". This difference can be used as the qualitative and possibly quantitative characteristic of the longitudinal diffusion and mixing, that is to say of the grain distribution, and thus, can serve as the flow characteristic of the detector in comparative tests.

Measurements of two kinds were undertaken: repeated scaler measurements (Fig. 4) and measurements with a ratemeter (Fig. 5). The shapes of the

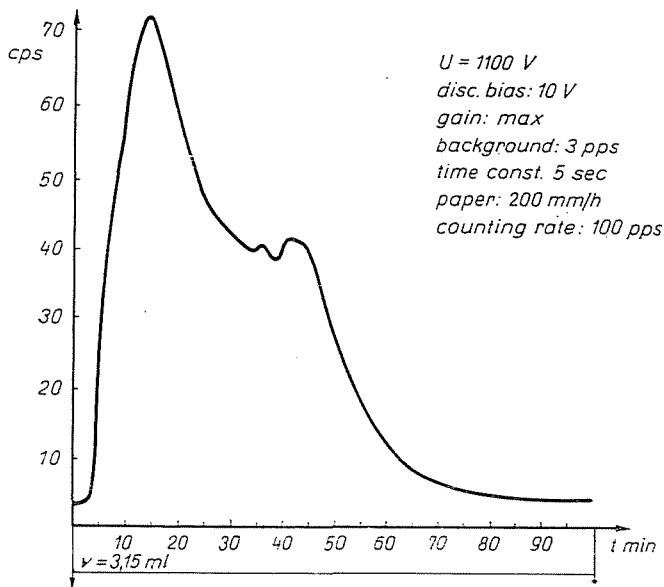


Fig. 5

curves obtained by the two methods are shown in the two figures. It will be seen that the character of the curves is identical, exhibiting an efficiency peak at the entrance section of the detector, and a similar but lower peak at the exit. Efficiency is lower in the middle of the detector. Obviously, this efficiency distribution can be attributed to two causes: to heterogeneous grain distribution and to a migration of the grains because of the alternations of the flow direction of the liquid at the pressure tests.

The shape of the curve permits to draw the following two conclusions:

a) the method described appears to be suitable for the examination of the anthracene particle distribution.

b) the volume of the sample must be larger than the volume of the detector, otherwise errors as great as 100 per cent may be incurred.

As was to be expected, the ascending branch of the curve was steeper than the descending one. The difference was not great, this finding being indicative of the slight degree of longitudinal mixing.

In the determination of the useful volume, we started from the presumption that the arrival and the departure of the front of the active plug are given by the starting points (points determined directly or by extrapolation) of the ascending and descending curves, respectively. (In the ideal case, the count/time — volume curve would be a rectangle.) The counting rate was measured in function of time and, simultaneously, the volume was determined in function of time. Within measuring errors, flow rate was constant, so that detector volume could be calculated directly.

On the basis of the results of nine measuring series (with ratemeter and with scaler, respectively), a detector volume of $0.35 \text{ ml} \pm 0.02 \text{ ml}$ has been obtained.

In these investigations, the error in the determination of volume and time was less than 1 per cent. The accuracy of the results was determined by possible changes in flow rate and by the accuracy of the extrapolation.

The detector was in operation for about a year. The average efficiency was practically constant during this period, while the efficiency distribution and the flow resistance of the detector did change. The increase in flow resistance could be compensated by a reversal of the flow direction. According to our experiences, however, with packings of inhomogeneous grain size it is recommended after one year, to fill the detector with a fresh packing.

As a conclusion, the following statements can be made:

The flow characteristics (flow resistance, mixing) of the flow chamber filled with anthracene powder are suitable for the initial requirements. According to our examinations, measuring times of 10 to 15 minutes can be ensured, which represent 30 to 50 per cent of the measuring time of a liquid scintillation counter without a sample exchanger.

Maximum efficiency is 40 per cent, for optimum signal/noise ratio the efficiency is 20—30% for S—35 and C—14 measurement.

Sulfite ions and dilute sulfurous acid solution do not perceptibly modify the parameters of the detector.

With the apparatus described, liquid samples of a volume of 0.4—0.5 ml can be measured continuously or discontinuously. In cases of radioindication, where no efficiency data are required, the minimum volume of sample will be determined by its specific activity.

It must be particularly emphasized that the detector described is suitable without the use of any special auxiliary equipment (special multiplier and scaler, cooling, etc.) for the detection of weak beta emitters at a high efficiency. Moreover, the detector can be prepared easily in any laboratory.

5. Plastic scintillation detector

For comparison, the properties of the plastic scintillator Tesla Model SPP 35 (Fig. 1 right) have also been investigated. This is a transparent plastic capillary bent helically, containing p-terphenyl and POPOP as active components. The full length of the capillary is about 1 m, its useful volume 0.5 cm^3 . It can be fitted readily to the Polish liquid scintillation apparatus Model SE—2, after a minor modification of the latter. Its photomultiplier Model EMI 9514 S was excellently suited for the measurements.

The original apparatus comprised only a scaler. This was completed by a Gamma ratemeter, equipped with a recorder. Thus, total activity and actual

activity could be measured simultaneously, the latter could even be recorded. This apparatus was also suitable for recording radiochromatograms. In this case the scaler functioned as an integrator. Though this plastic scintillator can be used for the detection of both gases and liquids, here measurements in the liquid phase will only be considered.

The efficiency of this detector is substantially lower than that of the anthracene powder detector, discussed in detail in the previous chapter. Its efficiency for S—35 in aqueous solutions is not more than 5 to 10 per cent. The lowest detectable activity, taking also the lower dark noise of the EMI

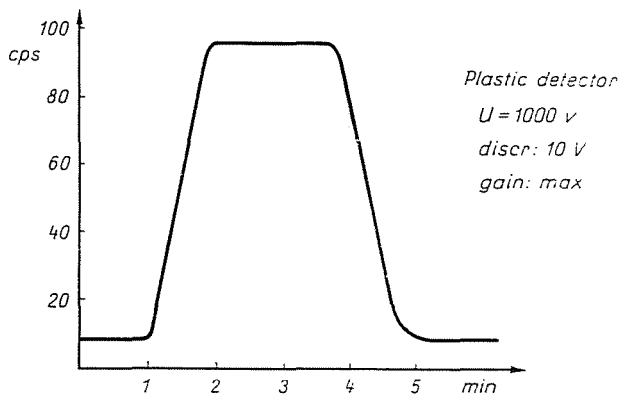


Fig. 6

multiplier into consideration, was about twice the value obtained with the anthracene powder detector, and would be about quadrupled with the same multiplier. This disadvantage is offset in most cases by other properties, provided the activities to be measured are not very low. The most important properties are the following:

a) There are no movable parts (anthracene powder), and therefore, efficiency and flow resistance are not affected by vibration or by a change in flow rate or flow direction.

b) No refilling from time to time is required, resulting in ease of handling.

c) Flow resistance is considerably lower, and thus, if necessary, relatively high flow rates may be used. Under these circumstances, the activity of high activity samples can be measured within 1 to 2 minutes.

d) The sensitivity of the spiral is uniform throughout its length. Peaks shown in Figs 4 and 5 are absent (Fig. 6). No error arises if the active sample does not fill completely the detector, or if the distribution of the activity is not uniform.

As for the other properties, there is no substantial difference between the two detectors. Also the plastic capillary does not bind the sulfur, and after

passing 1—2 ml of inactive solution through the detector, activity is reduced to the background level. Sulfite ions or sulfurous acid do not cause, with either of the detectors, any observable change in efficiency. Longitudinal mixing in the plastic detector is even less than in the anthracene detector, and an "activity-plug" of appropriate shortness gives a "chromatogram" having the shape of an isosceles trapezium (Fig. 6). It should be mentioned, however, that Figs 4 and 6 cannot be compared from this point of view, because flow rates differ considerably in the two cases.

6. Evaluation of the results

It has been concluded that both detectors investigated were suitable for the measurement of weak beta-emitter isotopes in aqueous solution. The efficiency of the anthracene detector is about four times that of the plastic detector, so that the anthracene detector seems to be the proper choice for low activity measurements. Moreover, it has the advantage that it can be prepared easily in any laboratory. With higher activities, in general, the use of a plastic scintillator is recommended, because this detector is easier to handle and has a higher stability. As against customary liquid scintillator solutions, here the presence of sulfur dioxide or sulfurous acid does not interfere. They can be used both for continuous and for discontinuous measurements. In discontinuous work, single determinations require 10—15 minutes, but when measuring higher activities, this period can be reduced to 1—2 minutes by increasing the flow rate, particularly in the case of the plastic detector.

If the sample is injected into an inactive liquid stream, the volume of the sample to be tested can range from a few tenth of microlitre to a few tenth of millilitre. Moreover, there is no obstacle of passing the whole of a greater volume of active sample through the detectors.

With the aid of the coupled recording equipment, both detectors are suited for radiochromatogram recording.

Summary

The possibilities of the direct measurement of the activity of weak beta-emitter isotopes (C—14, S—35) in aqueous solution have been studied. Detectors were to be found, with which sulfite ions or free sulfurous acid do not interfere.

Detectors of two types were studied in detail. One of them was a polyethylene tube bent helically, and filled with anthracene powder, the other a plastic scintillator capillary, also wound spirally. The advantages of the first type are its high sensitivity (20 to 40 per cent efficiency), the ease of preparing it in any laboratory, and the fact that its use does not require any special auxiliary equipment. Though of considerably lower efficiency (5 to 10 per cent), the second type, owing to its reliability and easy handling, can be used more generally, but it is more exacting as concerns apparatus. Both of the detectors can be used either for the determination of the activity of single samples, or for radiochromatogram recording.

References

1. NAGY, L. G.—TÖRÖK, G., SZARVAS, T.: *Per. Pol. Chem.* **10**, 279—302 (1966).
2. TÖRÖK, G.—SZARVAS, T.—NAGY, L. G.: *Per. Pol. Chem.* **12**, 229—243 (1968).
3. HAYES, N. *et al.*: *Nucleonics* **14**, 48 (1956).
4. GORDON, C. F.—WOLFE, A.: *Anal. Chem.* **32**, 574 (1960).
5. ROUCAYROL, J. C.—OBERHAUSER, E.—SCHNOSLER, R.: *Nucleonics* **15**, 104 (1957).
6. FUNT, B. L.—HETHERINGTON, A.: *Science* **131**, 1608 (1960).
7. SCHRAM, E.: *Organic Scintillation Detectors*. Elsevier, Amsterdam, 1963.
8. PINTÉR, K. G.—HAMILTON, J. G.—MILLERY, O. N.: *Anal. Biochem.* **4**, 458 (1963).
9. WEG, M. W.: *Nature* **194**, 180 (1962).
10. FUNT, B. L.—HETHERINGTON, A.: *Science* **129**, 1429 (1959).
11. KIMBEL, K. H.—WILLENBRINK, J.: *Naturwissenschaften* **45**, 567 (1958).

Dr. Gábor TÖRÖK
Dr. Gyula PARLACH
Dr. Lajos György NAGY

} Budapest XI., Budafoki u. 8—10, Hungary