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SOME THEORETICAL AND PRACTICAL ASPECTS OF THE USE OF RADIO GAS CHROMATOGRAPHS

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SUMMARY

Exact relations for the count rate and the count number have been derived which permit the specific activities of gas chromatographic peaks to be calculated for the case when the peaks are delayed but not distorted in the flow-type counting tube. For distorted peaks (large counting-tube volumes), no such calculations can be carried out. In agreement with literature data, it is shown that the optimum voltage applied to the counter can be found by use of external radiation sources. The measured count number is significantly affected by the composition of the counting gas; as regards the efficiency of the counting, there is an optimum gas composition, where the count number is at a maximum (the other parameters affecting the counting being kept constant). Under otherwise identical conditions, the width of the gas chromatographic peak has no effect on the observed count number, and thus the activities of narrow and wide gas chromatographic peaks can be evaluated equally well.

INTRODUCTION

The coupling of gas chromatographic (GC) separation with radiation detection is a new and promising technique due to Emmett and co-workers[1]. Advances in handling the difficult task of radioactive assay of soft β-emitters in the gas phase[2–9] has led to the development of proportional counting tubes and appropriate techniques which were first used in a steady-state mode[10–20]. A very sensitive through-flow type detector is now available for radio gas chromatography (RGC).

As regards high efficiency in the counting of soft β-emitters, through-flow type proportional counting tubes retain the advantages of static devices while operating continuously. For this reason these detectors are being increasingly used in the assay of the radioactivity of labelled GC components, and the detectors are also the subject of intensive research in order to find the optimum parameters for their operation[21–30]. However, although many papers have dealt with different aspects of practical applications of these detectors[31–44], the underlying principles have not been completely elaborated.

All of the studies on through-flow type counting tubes refer to the work of Wolfgang and Rowland[22], who characterized these tubes in a fairly intuitive manner:

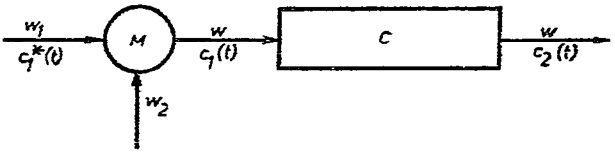

Fig. 1. Model of the counting tube: M = gas mixer; C = counting tube.

the measured number of counts is proportional to the tube volume and inversely proportional to the rate of flow of the gas mixture. By administering various gas impulses, Rowland and his co-workers[38] measured the decrease in efficiency as a consequence of the deterioration of the composition of the counting gas. In these experiments use was made of an external γ-source, and the commercial radio gas chromatographs are probably calibrated with external radiation sources[38,44].

One aim of the present paper is to determine the conditions under which Rowland's intuitive conclusions, regarding the counting rate, are valid, and to distinguish modes of operation for which they are invalid. A comparison has also been made between an external γ-source and an internal β-emitting substance flowing through the tube, concerning the differences to be expected in the tube characteristics and the dependence of the efficiency on the composition of the counting gas.

THEORETICAL CONSIDERATIONS IN CONNECTION WITH THE RATE OF COUNTING

For simplicity, let us consider the following model. A substance of specific activity A (disintegrations/sec·mole) arrives with a flow-rate w_1 (cm^3/sec) and a concentration distribution $c_1^*(t)$ (mole/cm^3) at a gas mixer M (see Fig. 1) where it is mixed with a counting gas (*e.g.*, methane) of flow-rate w_2. The gas mixture of concentration $c_1(t)$ and flow-rate $w = (w_1 + w_2)$ then enters a counting tube of volume V (cm^3). The flow-rate of the gas leaving the tube is also w.

Let us assume that the inlet concentration profile, $c_1(t)$, is unchanged throughout the counting tube. The role of the tube is only to cause a time delay, Δt. The background radiation is disregarded, and an initial point in time, t_0, is selected at which the counting tube does not contain active material, and thus it holds that:

$$c_1(t_0) = 0 \text{ and } c_1'(t_0) = c_1''(t_0) = \ldots = 0 \tag{1}$$

Let us determine the count rate, $r(t)$ (count/sec), under these conditions. The frequency of the counts is proportional to the amount, $n(t)$ (mole), of the radioactive substance in the counting tube. The proportionality factor is the specific activity, A, but this gives only the number of disintegrations ensuing and must be multiplied by the efficiency factor, k, characteristic of the counting tube in order to obtain the count rate:

$$r(t) = k \cdot A \cdot n(t)$$

In agreement with the preliminary assumptions, the content of the active material in the counting tube at time t is given by the following relation

$$n(t) = \int_{t_0}^{t} [\dot{n}_1(\tau) - \dot{n}_2(\tau)]\mathrm{d}\tau$$

where $\dot{n}_1(t)$ and $\dot{n}_2(t)$, the inlet and outlet material currents (mole/sec), respectively, can be calculated from the relations:

$$\begin{aligned} \dot{n}_1(t) &= w_1 \cdot c_1^*(t) = w \cdot c_1(t) \\ \dot{n}_2(t) &= w \cdot c_2(t) \end{aligned} \tag{2}$$

Taking eqns. 2 into consideration, the count rate can be written as follows:

$$r(t) = k \cdot A \cdot w \cdot \int_{t_0}^{t} [c_1(\tau) - c_2(\tau)] \mathrm{d}\tau$$

If, in accordance with the original assumption, it is true that $c_2(t)$ is equal to $c_1(t)$, but merely delayed by time Δt, then:

$$c_1(t - \Delta t) = c_2(t)$$

If $c_1(t - \Delta t)$ is expanded into a series of t, then the expression for $r(t)$ can be rewritten in the following way:

$$r(t) = k \cdot A \cdot w \cdot \int_{t_0}^{t} \left[c_1(\tau) - \sum_{j=0}^{\infty} (-1)^j \cdot \frac{c_1^{(j)}(\tau)\, \Delta t^j}{j!}\right] \mathrm{d}\tau \tag{3}$$

Delay only

It can be very easily shown that eqn. 3 can be simplified to

$$r(t) = k \cdot A \cdot V \cdot \left[c_1(t) - \frac{c_1'(t)\, \Delta t}{2!} + \frac{c_1''(t)\, \Delta t^2}{3!} - \ldots\right] \tag{4}$$

because t_0 was selected so as to ensure that the condition $c_1(t_0) = c_1'(t_0) = \ldots = 0$ is fulfilled. Δt is the mean value of the residence time of the radioactive substance in the counting tube: $\Delta t = V/w$.

If eqn. 4 is integrated between the limits t_0 and t_1 (again t_1 is chosen so to satisfy the condition 1) we obtain the total number of counts observed in this time interval

$$R(t_0,t_1) = k \cdot A \cdot V \cdot \left\{\frac{N}{w} - \frac{\Delta t}{2!}[c_1(t_1) - c_1(t_0)] + \frac{\Delta t^2}{3!}[c_1'(t_1) - c_1'(t_0)] - \ldots\right\} =$$

$$= \frac{k \cdot A \cdot V}{w} \cdot N \tag{5}$$

where $N (\equiv w \int_{t_0}^{t_1} c_1(t) \mathrm{d}t)$ is the amount of the radioactive substance in moles which enters the counting tube in the time interval (t_0,t_1). Eqn. 5 is the exact relation for the count number in the time interval (t_0,t_1), when the impulse only undergoes delay in the counting tube. It is to be noted that, by suitable choice of the initial and final points of counting, the total number of counts is independent of the shape of the GC peak.

For counting tubes of very small size ($\leqslant 2$ cm^3) and/or relatively large volumetric flow-rates, the counting rate (eqn. 4) is fairly well represented by the first member of the series provided that the first and higher derivatives do not exceed a properly selected upper limit:

$$r(t) = k \cdot A \cdot V \cdot c_1(t) = \frac{k \cdot A \cdot V \cdot w_1}{w} \cdot c_1^*(t) = \frac{k \cdot A \cdot V}{w} \cdot \dot{n}_1(t) \tag{6}$$

For the determination of the specific activity of a given chromatographic peak, the integral mode of operation (*i.e.*, when we record the total number of impulses produced in the time interval $[t_0, t_1]$) is the most suitable (eqn. 5), provided that N is known from independent measurements.

Relations 4 and 6 are merely theoretical possibilities, for, in the case of the differential measuring mode, the specific activity is determined via "the area under the curve" from ratemeter records. In both differential and integral modes of operation, the value of the product kV should be established by calibration experiments.

Delay and distortion

If eqn. 1 is written in the form

$$n(t) = N_1(t) - N_2(t)$$

where N_1 and N_2 are the amounts (in moles) of active material entering and leaving the counting tube over the period t_0 to t, it is readily seen that, even in the case of the knowledge of some analytical properties relating to $N_1(t)$ and $N_2(t)$, $n(t)$ and consequently its integral (to which $R(t_0,t_1)$ is proportional) can be very complex; accordingly, no definite statement can be made with regard to $R(t_0,t_1)$. In our view (in counting tubes of sufficiently large volume), some practical importance may be attributed to the case where the tube takes up the entire material impulse without simultaneously emitting radioactive material.

Considering the successive appearance of several radioactive components, which is often the case in actual chromatographic separations, the commercial counting tubes only satisfy the above condition at randomly. In theoretical research with one radioactive component, however, the condition can certainly be fulfilled.

EXPERIMENTAL

The experiments were carried out with a Perkin-Elmer RGC-170 instrument with two counting-tube accessories with nominal volumes of 2 and 10 cm^3. The counting gas was a mixture of nitrogen and methane.

The efficiency factor was studied as a function of the composition of the gas mixture, of the voltage supplied to the counting tube and of the volumetric flow-rate of the counting gas. In the experiments performed with a closed, external, ^{90}Sr radiation source, the counting time was 15 sec in all cases. In the experiments with $^{14}CO_2$, the amount of labelled material (specific activity, 19.7 mCi/mole) added to the stream of nitrogen carrier gas from a sample loop was $4.01 \cdot 10^{-6}$ mole in all of the measurements. The methane gas was supplied at different flow-rates and was mixed thor-

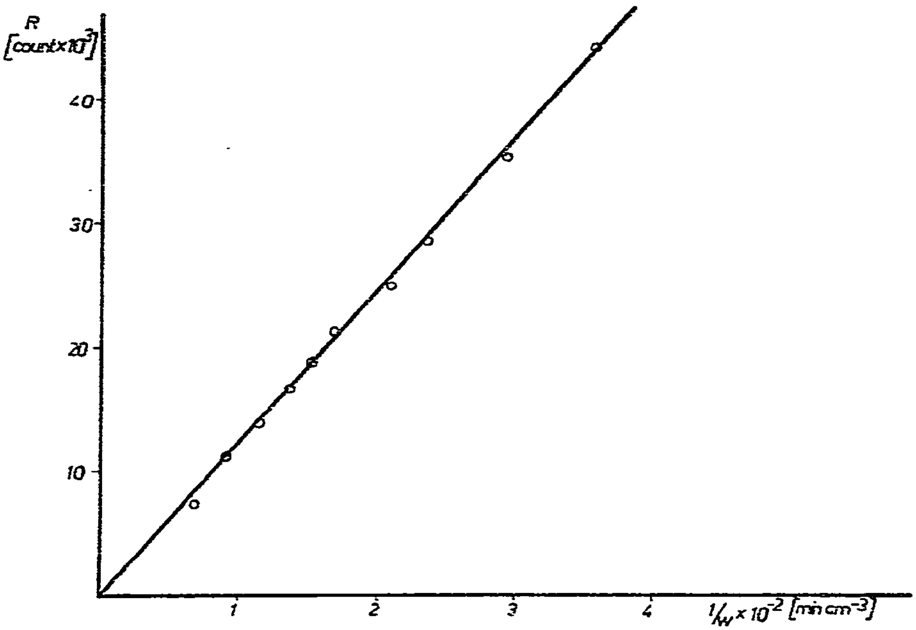

Fig. 2. Variation of the count number, R, at different flow-rates, w. $V = 10$ cm^3, $U = 3100$ V and $x_M = 50.2 \pm 0.3\%$.

oughly with the carrier gas in a mixer before entering the counting device. The flow-rates for both gases were stabilized carefully and measured.

Examinations of the characteristics with closed external ^{90}Sr and internal $^{14}CO_2$ radiation sources

When an external radiation source is used, the integral count number $R(t_0,t_1)$[*] must in principle be independent of the flow-rate, w, of the gas mixture, and this was found to be so in practice. In agreement with the earlier results of a number of workers[22,23], we found that the voltage U(V)–gas mixture composition x_M (%)[**]–count number R [count] surface exhibits an almost horizontal plateau, which broadens with increasing methane concentration. The projections on to the x_M/U plane of the plateaus, determined for counting tubes with volumes of 2 and 10 cm^3, coincided very well. From these investigations, it is concluded that $U = 3100$ V is the optimum operating voltage over a wide range of methane concentrations.

When radioactive carbon dioxide was used as the internal radiation source, it was found that, as for the external characteristics, over a wide range of composition of the counting gas the optimum voltage of the counting tube was 3100 V.

Effects of varying the flow-rate, w, and the methane concentration, x_M

With U fixed at 3100 V and x_M fixed at 50 or 66%, experiments were carried out in which the flow-rate, w, was varied in the range 10–200 cm^3/min. On increasing

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[*] For simplicity, R [count] will be used instead of the notation $R(t_0, t_1)$ [count].

[**] x_M (%) means the concentration of methane in the nitrogen carrier gas.

TABLE I

DEPENDENCE OF THE PRODUCT OF THE EFFICIENCY AND THE SPECIFIC ACTIVITY (kA) ON THE FLOW-RATE OF GAS MIXTURE

10-cm³ counting tube			*2-cm³ counting tube*		
Flow-rate, w (cm³/min)	*Methane concentration, x_M (%)*	*Efficiency·specific activity, $kA \cdot 10^5$ (count/mole·min)*	*Flow-rate, w (cm³/min)*	*Methane concentration, x_M (%)*	*Efficiency·specific activity, $kA \cdot 10^5$ (count/mole·min)*
27.9	50.8	308.52	29.5	48.8	299.25
34.3	51.6	301.59	39.5	50.1	291.61
42.1	48.7	300.38	44.4	50.0	261.81
47.6	48.8	296.55	49.2	50.0	275.57
60.0	51.7	318.65	60.0	50.9	270.37
66.6	50.0	313.76	66.6	50.8	292.82
73.1	51.9	305.52	82.2	49.9	236.25
85.7	49.3	296.75	92.3	50.0	261.93
109.1	49.9	299.47	133.3	50.0	253.50
148.1	49.3	283.36	157.8	50.6	230.00
	50.2 ± 1.1	302.5 ± 9.2		50.1 ± 1.7	267.3 ± 20.6
21.4	66.2	250.37	22.0	65.5	269.73
26.4	66.9	244.73	29.5	67.0	269.94
31.2	65.7	268.78	33.3	66.6	266.26
34.4	67.4	251.45	37.8	64.9	256.10
43.5	66.6	265.38	44.7	65.6	243.38
50.8	65.5	273.13	54.1	62.7	259.84
59.4	63.9	273.44	60.0	68.7	218.97
65.9	64.1	250.89	74.1	62.3	252.04
90.9	60.0	268.29	101.6	65.5	235.24
111.1	65.8	247.88	115.4	69.3	225.51
	65.2 ± 2.1	259.4 ± 10.7		65.5 ± 2.1	249.6 ± 17.4

TABLE II

DEPENDENCE OF THE INTEGRAL COUNT NUMBER ON THE METHANE CONCENTRATION

Methane concentration, x_M (%)	*Integral count number, R (count)*
8.7	20115 ± 225
14.6	22746 ± 158
24.8	25459 ± 225
38.4	27630 ± 223
42.3	26470 ± 286
49.1	27230 ± 175
58.2	26070 ± 143
65.7	24320 ± 149
71.1	20070 ± 120
77.1	17770 ± 595

TABLE III

DEPENDENCE OF THE INTEGRAL COUNT NUMBER ON THE HALF-WIDTH OF THE GAS CHROMATOGRAPHIC PEAK

Half-width of GC peak (s)	*Integral count number, R (count)*
1.3	14430
1.9	14683
4.7	14360
6.0	14783
6.2	14340
6.7	14400
	14501 ± 166

the flow-rate, w, the count number, R, decreased as shown in Fig. 2, where R is represented as a function of the reciprocal of the flow-rate ($1/w$) under the conditions $V = 10$ cm^3 and $x_M = 50.2\%$.

According to relation 5, the product $[R(t_0,t_1)w]/[V\cdot N]$ (count/mole·sec) should be independent of the flow-rate, w, of the gas mixture. This is shown to be so in Table I. It can clearly be seen from Tables I and II that the efficiency of the 10-cm^3 tube is nearly 80% at the optimum methane concentration. The efficiency of the 2-cm^3 tube is only a few percent less. From Table II it follows that the efficiency of counting depends on the methane concentration, x_M, in the counting gas. The maximum efficiency is attained at an intermediate value of the composition. In our case this maximum could be observed at $x_M = 42.5\%$. Table II also shows the count numbers, R, for a wide range of methane concentration ($8.7 \leqslant x_M \leqslant 77.1$) for the 10-cm^3 counting tube, with U fixed at 3100 V and w fixed at 41.4 cm^3/min; *i.e.*, in essence, it shows the effect of varying x_M.

Effect of the form of $c_1^*(t)$

In conclusion, a study was made of whether the integral count number, R, depends on the "width" (dispersion) of the GC peak. In these experiments, ^{14}C-labelled propylene was used. In each experiment, $2.4\cdot10^{-6}$ moles of propylene were added to the nitrogen carrier gas. A series of peaks of various widths were produced by increasing the length of the GC column, and the corresponding count numbers were measured. The examinations were carried out under the following conditions: $U = 3100$ V, $w = 30$ cm^3/min, $x_M = 40\%$ and $V = 10$ cm^3.

Table III shows the integral count numbers, R, as a function of the half-widths of the peaks. It can be seen that the width of the GC peak (the form of $c_1(t)$) does not influence the value of R, as was also demonstrated theoretically.

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