The validity of the results obtained when a stream-splitting device is used before the gas-liquid chromatography detector

ARTHUR KARMEN, IRMGARDE MCCAFFREY, and ROBERT L. BOWMAN

Laboratory of Technical Development, National Heart Institute, Bethesda 14, Maryland

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» We have previously reported using several different approaches to the radioassay of components in the effluent of a gas-liquid chromatographic column (1–4). In this work we found it convenient to record the mass of the components by the use of ionization detectors because of their simplicity and high sensitivity, and particularly because of their relative insensitivity to small temperature changes. Each of the ionization detectors, however, has at least one of several features that might cause difficulty. Different ionization detectors might destroy the sample, or dilute it with large volumes of other gases, or contaminate it with radioactivity, or provide sufficient penetrating radiation to make operation of a sensitive radiation detector in the close vicinity difficult. Most of these difficulties might be avoided by dividing the effluent of the column

into two parts, the smaller of which is diverted to the mass detector while the larger is used for the radioassay.

A device for dividing the effluent is easily constructed. A procedure we have used several times has been to drill a $^1/_{16}$-in. diameter hole along the axis of a 1-in. long, $^1/_4$- to $^1/_2$-in. diameter stainless steel cylinder; and a $^1/_{16}$-in. diameter hole in the side of the cylinder to meet the axial hole. A stainless-steel tube is silver soldered into each of the three orifices of the T connection thus formed. A $^1/_{16}$-in. o.d., thin-walled, stainless-steel hypodermic tube soldered in one end of the cylinder forms the gas inlet. Two lengths of capillary tubing, 0.010 in. i.d., $^1/_{16}$ in. o.d., one 1 in. long, the other 8 in. long, are used as outlets. The lengths of the outlets are generally chosen to be in inverse ratio to the division desired but final adjustment is made by constricting either tube slightly using diagonal cutting pliers. The rates of carrier gas flow in each limb are then determined and the quantity of radioactivity assayed is corrected, if desired, for the small fraction used for mass detection.

The validity of the assumption that when the carrier gas is divided in a given ratio, each of the individual components being analyzed will likewise be divided in the same ratio or a constant ratio is open to question. The resistance to flow offered by each outlet tube is a function of the flow rate of gas in the tube and the viscosity of the gas as well as of the cross-sectional area of the tube or of the constrictions. Since the viscosity of the gas as well as the flow rate might undergo changes during the course of the elution of a component, the fraction sent through each outlet might vary. It was interesting, therefore, to evaluate the magnitude of the resulting errors.

A stream-splitting device was constructed as described. It was adjusted until the flows through the exit tubes were in the ratio of approximately 10:1. The device was then placed in a detector oven of a gas chromatograph. Its inlet was connected to the outlet of a gas-liquid chromatography column (glass, 4 mm i.d., 5 ft long, filled with Chromosorb W [Johns-Manville Corp., NYC], 90%, coated with ethylene glycol adipate polyester, 10%). Each outlet was connected to the heated inlet of separate Packard Instrument Co. Model 830 gas fraction collectors. Each of the two fractions of the effluent was thus passed through similar cartridges containing anthracene crystals coated with silicone oil for collection and radioassay of components (4). No mass detector was used in these experiments since the column had been used previously at similar pressures and temperatures and its retentivity for methyl esters was known. A series of 5-μl samples of a solution of C^{14}-labeled methyl laurate containing less than 1 μg of methyl ester was injected. Following each injection, the entire effluent of each limb of the stream splitter was collected in a single cartridge. A second series of samples, containing the same amount of radioactivity plus 1 mg of carrier methyl laurate in the 5 μl, was then injected into the column, fractionated, and collected similarly. The flow rate through each tube was determined in triplicate both before and after each analysis using a soap bubble flowmeter. The average value was used. The radioactivity in each cartridge was determined by scintillation counting as described previously (4).

TABLE 1. COMPARISON OF THE DIVISION OF CARRIER GAS FLOW BY THE STREAM-SPLITTING DEVICE WITH THE DIVISION OF C^{14}-METHYL LAURATE VAPOR IN THE GAS*

Sample No.	Carrier Gas Flow (cc/min) A	B	Splitting Ratio A:B	Methyl Laurate Radioactivity (cpm) A	B	Splitting Ratio A:B
1	6.6	53.5	1:8.1	7,926	63,801	1:8.05
2	6.6	55.5	1:8.4	7,882	67,172	1:8.52
3	6.6	55.5	1:8.4	7,370	61,648	1:8.36
4	6.6	55.5	1:8.4	7,686	65,031	1:8.48
5	6.6	55.5	1:8.4	7,967	66,074	1:8.30
6	6.5	53.6	1:8.2	8,047	65,312	1:8.12
7	6.5	53.6	1:8.2	7,923	64,597	1:8.16
8	6.5	53.6	1:8.2	7,716	62,694	1:8.14
9	6.5	53.6	1:8.2	8,615	67,954	1:7.89
10	6.5	53.6	1:8.2	7,569	65,580	1:8.66
11	6.5	53.6	1:8.2	7,963	66,399	1:8.33
12	8.5	63	1:7.4	7,891	59,975	1:7.60
13	9.7	70.6	1:7.4	8,916	67,214	1:7.55
14	12	86	1:7.2	9,530	68,511	1:7.20

* Each injection consisted of 5 μl of a solution of C^{14}-methyl laurate in trimethyl pentane. Injections 1–6 contained less than 1 μg of methyl laurate; 7–11 contained 1 mg; 12–14 show the effect of increasing the total flow of gas. Assayed by liquid scintillation counting at the same voltage, 5 μl contained 76,000 cpm (100,000 dpm).

The results are tabulated in Table 1. Within the limits of accuracy of the flow measurements and radioassay, no difference was detected at any of the flow rates tested between the division of carrier gas flows and the division of components, whether the component was low in total mass or whether the concentration of methyl esters in carrier gas was close to the upper limit for this type of column. It should be noted that the ratio of the flow rates in the outlet limbs of the stream divider did not exceed 10:1. A difference between the ratio of carrier gas division and the ratio of component division might be expected to be more evident if the gas stream were divided 100:1 or 1000:1, but we have not determined this.

The device that was used offered sufficient resistance to flow in both limbs so that insertion or removal of an anthracene-filled vial in one limb did not alter the flow in the other limb. This property is necessary if the stream-dividing device is to be used followed by any equipment that itself offers a small resistance to flow. As shown in the table, the fraction flowing through each limb was changed by changing the total flow. This finding suggested that the flow through each limb should be determined under actual operating conditions. Since changing the total flow rate of gas changed the splitting ratio, a change in flow rate during the course of an analysis thus is a potential source of error. A significant change in flow rate might be produced by a change in the temperature of the column during the analysis unless care is taken to avoid large changes in flow.

The effect of change in the composition of the gas from argon to argon plus low concentration of methyl laurate to argon plus higher concentrations of methyl laurate was insufficient to produce a measurable change in splitting ratio. It was thought unlikely, therefore, that other methyl esters of fatty acids or other compounds analyzed by gas chromatography when present in ordinarily expected concentrations in the gas would produce a sufficiently greater change in viscosity to produce a different splitting ratio, and we have not explored this possibility.

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