Note

Diffusion in the bubble flow meter in inverse gas chromatography experiments

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In gas chromatography (GC), the simple method of measuring the flow-rate by means of a soap bubble flow meter is still considered to be the most reliable and error-free. In this method, a measured gas ascends a calibrated tube; the ascent is followed by observing a movement of a thin layer of soap solution (the bubble) introduced into the tube: the linear velocity of the bubble is measured.

During our studies of the thermodynamic behavior of polymer–solvent systems using inverse GC, we have measured the dependence of the retention volume of the marker (methane) on the flow-rate of the carrier gas (helium). While no dependence was expected, our data exhibited a significant decrease at the low flow-rates (Fig. 1).
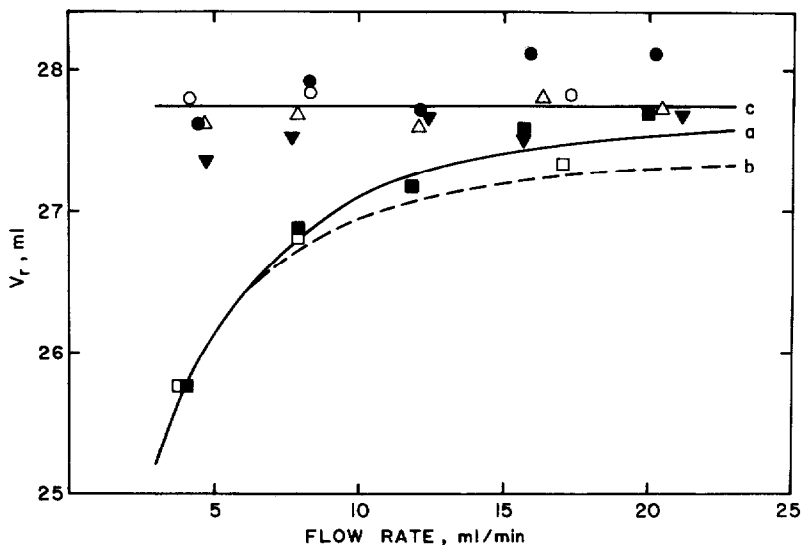

Fig. 1. The effect of flow-rate on marker retention volume: column with 7% poly isobutylene (■) before correction and (●) after correction (0.3 ml); (□) second set of data before correction; (○) second set of data after correction; (△) data obtained using nitrogen as a carrier gas; and (▼) data obtained using the new bubble flow meter. Line a was drawn through the uncorrected experimental points. Line b is an idealized experimental dependence that would yield, after correction, data independent of flow-rate (line c).

Similar results were observed earlier by Czubryt and Gesser[1]. The reduction of the retention volume reached almost 10% at our lowest flow-rate, 4 ml/min. The retention volumes of the other solutes (probes) were reduced proportionally. We observed this behavior for a number of columns loaded with different materials. Similar phenomena were observed by Dincer and Bonner[2].

We were able to trace the discrepancy to an improper measuring technique of the flow-rate. An analysis of our experimental results suggested that we are underestimating the flow-rate by a small amount: this amount was independent of the flow-rate and consequently had the largest relative importance at low flow-rate. It was caused by diffusion of helium through the bubble.

In this note, the erroneous flow-rate measurements are described and analyzed. A modified design of the soap bubble flow meter is developed for accurate measurement of the flow-rate when a carrier gas other than nitrogen (*e.g.*, helium) is used.

EXPERIMENTAL

Measurements were made on a modified Varian Aerograph Model 2100-40 gas chromatograph equipped with a flame ionization detector. Dried helium was selected as a carrier gas. The flow-rate was controlled by a precision needle valve and measured by a 50-ml thermostated soap bubble flow meter. The flow-rate was monitored frequently by taking an average of three readings every time; these readings usually agreed within 0.5%. The inlet and outlet pressures were monitored frequently by a mercury manometer. The inlet pressure was generally in the range of 900 mmHg (total pressure) while the outlet pressure was always atmospheric. Methane gas was used as a marker for retention time. The three columns used in this study were composed of Chromosorb W, AW DMSC treated, with (1) no polymer coating; (2) 7% poly isobutylene coating; and (3) 7% poly(methyl acrylate) coating. The detailed procedure of coating these polymers onto the support is reported elsewhere[3].

A constant amount of marker was injected and the retention time measured at the peak maximum. The retention volume was then calculated using the relationship

$$V_r = t_m F f(P)(T_c/T_f) \tag{1}$$

where V_r is the retention volume of marker (in ml), t_m is the retention time of marker (in min), F is the flow-rate (in ml/min), $f(P)$ is a pressure correction factor calculated according to eqn. 2, and T_c and T_f are the column temperature and flow meter temperature, respectively. The pressure correction factor was calculated as[4]

$$f(P) = \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{2}$$

where P_i and P_o are the pressures at column inlet and outlet, respectively.

In our early measurements, a bubble flow meter of usual design was used. The design was later modified by the addition of an inverted U-tube to the outlet of the bubble flow meter. A second inlet at the bottom of the flow meter was used for flushing the meter with helium before starting the flow measurement. During the measurement, this inlet was closed by a valve (Fig. 2).
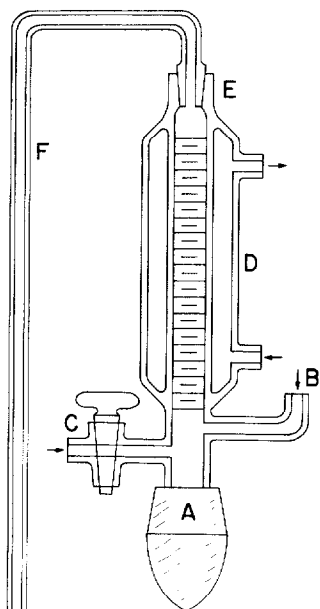
Fig. 2. New design of soap bubble flow meter: A, soap solution reservoir; B, the incoming helium gas from the column; C, inlet valve for fast flushing of the bubble meter by helium gas; D, thermostated bubble meter; E, ground joint; and F, inverted U-tube, 1/8 in. I.D.

RESULTS AND DISCUSSION

The following experiments were performed to check the usual method of measuring the flow-rate. The standard design of the bubble flow meter was used.

(1) A bubble was introduced into the measuring tube of the flow meter at some flow-rate and then the flow of helium was cut off. After the pressure gradient across the column vanished, the bubble started receding at a velocity of about 0.3 ml/min.

(2) In a similar experiment, a number of bubbles were introduced. All the bubbles were receding, but the top bubble receded much faster than the bottom one. The volume between bubbles decreased by about 10% over 20 min.

These results can be explained by the diffusion of helium upwards through the bubble. The amount crossing the membrane rises through the atmosphere and is replaced by heavier air. Thus the composition difference across the bubble is maintained and the diffusion current continues at an essentially constant rate. Conversely, when the air diffuses downwards through the bubble, then the air descends the tube: essentially pure helium is maintained under the bubble. The diffusion constant of helium is higher than that of air, resulting in a net flow out of the enclosed volume of helium and in a receding movement of the bubble.

The foregoing analysis was confirmed by the following experiments:

(1) Nitrogen, instead of helium, was used as a carrier gas. The diffusion constant of nitrogen is essentially the same as that of air. Accordingly, no movement was observed in the stop-flow experiment.

(2) Using nitrogen as a carrier gas, the dependence of the marker retention

volume on the flow-rate was measured. Retention volumes were constant within 1%
(Fig. 1).

(3) The original retention time data (using helium as a carrier gas) were corrected by adding 0.30 ml/min to the measured flow-rate. The corrected data were again constant within 1% (Fig. 1).

While the correction procedure produced reasonable and internally consistent data, it still proved to be a nuisance. Furthermore, an auxiliary measurement (the net diffusion flow) was needed; this introduced an unnecessary source of experimental error. We therefore made some simple changes in the design of the bubble flow meter. The new design is based on the expectation that no net flow will be observed if pure helium is contacting the bubble from both sides. Thus the escape of helium from the bubble meter must be prevented. This was easily accomplished by attaching an inverted U-tube to the top of the bubble meter and purging the bubble meter with a strong stream of helium before starting the flow measurement (Fig. 2).

In experiments using helium and the newly designed flow meter, no flow was observed in the stop-flow experiment. The retention volumes of the marker were independent of the flow-rate, and no flow correction was necessary (Fig. 1). At the high flow-rates, the corrected data in one set of measurements are too high by about 0.3 ml. We consider this error to be a random experimental error, perhaps due to an error in time reading. (An error of 0.02 min in the marker retention time would explain the discrepancy.) At low flow-rates, this error has found to be much less. In conclusion, the retention volumes when corrected for diffusion effects within the bubble meter, as well as those obtained by using the new design of the bubble meter, are independent of the flow-rate within ± 1%; this seems to be our random experimental error.

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