# NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(7), 1791—1792 (1974)

## High-precision Flow Meter for Gas Chromatography

Yoshio HORI* and Riki KOBAYASHI

*Department of Chemical Engineering, Rice University, Houston, Texas 77001, U.S.A.*

(Received September 28, 1973)

**Synopsis.** A gas-chromatographic apparatus with an empty tubing in place of a packed column can be used as a flow meter. The detector signal, processed by a differentiator-timer system, gives a precision of 0.06% in the measurement of the flow rate.

Gas chromatography in physico-chemical application requires precise measurements of the retention volume. Sources of error in the measurements of retention time have been analyzed, and various improvements have been made.[1-2] On the other hand, a soap film flow meter has been conventionally used for the measurement of the carrier-gas flow rate. Because of the visual observation of the soap film motion, the experimental uncertainty in the retention volume is at least 0.2—0.5%. No flow-measuring device can give much more precise measurements.

During the gas-chromatographic studies of physical adsorption and gas-liquid equilibrium at elevated pressures, a new flow meter was developed in this laboratory to give more precise measurements.

### Apparatus

*High-pressure Gas-chromatographic Apparatus.* The main features of the equipment are similar to those described previously.[3] Two high-pressure regulators made by the Matheson and Grove Valve & Regulator Co. were connected in series; they held such a constant pressure of the carrier gas that no change was detected in the Heise Gauge during any experimental run. The pressure was measured by means of Heise Gauges with certified accuracy of 0.1% of the full scale. Their ranges were 200, 1000, and 2000 psi. The pressure was kept constant at all experimental conditions (up to 120 atm) between the inlet and the expansion valve; the pressure drop across the packed column is negligible, as has been verified previously.[3] The pressure of the carrier gas is reduced to 1 atm at the expansion valve.

*Flow-measuring Device.* In a common gas chromatographic apparatus, a packed column can be replaced with an empty tubing of a known volume. Then one can obtain a definite retention time in accordance with the flow rate. This is the principle of the present flow meter.

A six-way linear gas-sampling valve manufactured by Varian Aerograph was used as the perturbation gas-injection valve. The volume of the sample loop of the valve was 0.18 ml. Two sets of copper tubing 1/4 inch in diameter were used as the empty tubing; one was 2 m long, and the other, 8.6 m long. Either of the two empty tubings was used according to the flow conditions. The pressures at both the inlet and the outlet of the empty tubings were measured by means of manometers filled with water. A Gow-Mac thermal conductivity cell (Model 10-460, Flo-thru type) was used. The flow-meter system was immersed in a thermostat, filled with silicone oil and maintained at 35.0± 0.03 °C.

The flow-meter system was connected to the outlet of the high-pressure gas-chromatographic apparatus. The flow-meter system is regulated at the constant temperature (35 °C), and the pressure in the empty tubing is measured (atmospheric pressure), so that the flow meter can work under any experimental conditions of the high-pressure equipment.

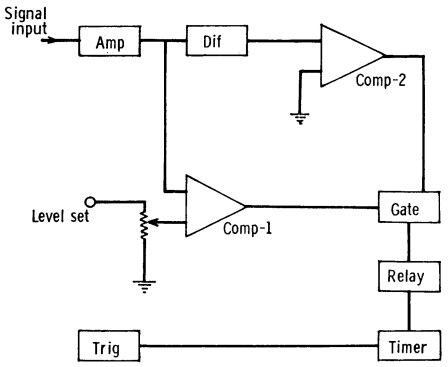


Fig. 1. Block diagram of the differentiator-timer system.

After the carrier-gas (methane) flow reaches a steady state, a dose of perturbation gas (argon) is injected by means of the sample injection valve, which triggers a microswitch at the same time. Then the timer starts. The perturbation gas, passing through the empty tubing, reaches the detector. The signal from the detector is differentiated by the differentiator and is compared with zero level by means of the comparator-2 (Fig. 1). When the elution peak reaches its maximum, the differentiated signal becomes zero, the relay system being driven to turn off the timer. The timer stops only when the input signal exceeds the preset threshold level (comparator-1) and the differentiated signal reaches zero. The timer, a Model S-6 Precision Timer manufactured by the Standard Electric Company, gives readings as precise as 1/1000 minute.

The present flow meter was calibrated against a soap-film flow meter, the volume of which had previously been calibrated. The retention time, $t$ (min), is related to the carrier gas flow rate, $f$ (cm³/min) (at 35.0 °C, atmospheric pressure), and the effective volume between the injection valve and the detector cell, $v$ (cm³):

$$f \cdot t = v + f \cdot \Delta t \qquad (1)$$

where $\Delta t$ (min) is a constant. $\Delta t$ corresponds to the delay in the detector system and the variation in the flow pattern according to the flow rate. The linear relationship (1) was found to hold for flow rates less than 180 cm³/min, using an

* Present address: Research Department, Kikumoto Works, Sumitomo Chemical Co., Ltd., Niihama, Ehime *792*.

appropriate one of the empty tubings (2 m and 8.6 m long). The *accuracy* of the present flow meter depends upon that of the soap-film flow meter. However, the *precision* is much improved, as is exemplified below.

## Results of Measurements

A lot of flow measurements were made for each experimental run by means of the present flow meter. Some of them are tabulated in Table 1. The retention times in the third line were obtained during the time shown in the fourth line. The constancy of the measurements is excellent.

Table 1. Reproducibilty of the measurements of flow rate

| | | | |
|---|---|---|---|
| Chromatographic pressure in the high pressure part[a] (atm) | 3.0 | 10.5 | 15.5 |
| Average flow rate at 35.0 °C, latm ($cm^3$/min) | 12.539 | 36.754 | 62.385 |
| Measured retention time by the flow meter (min) | 3.3109 | 1.1329 | 0.6701 |
| | 3.3114 | 1.1331 | 0.6692 |
| | 3.3117 | 1.1331 | 0.6701 |
| | 3.3113 | 1.1332 | 0.6701 |
| | | 1.1331 | 0.6698 |
| | | 1.1330 | 0.6698 |
| | | 1.1322 | 0.6701 |
| Duration in which the measurements were made (min) | 39 | 25 | 34 |

a) The flow meter is connected to the outlet of the high pressure gas chromatographic apparatus. The pressures before the expansion valve in high pressure apparatus are shown here.

According to the series perturbation technique,[3-6] the adsorption of methane on Porasil was precisely measured by means of a high-pressure gas chromatograph equipped with the present flow meter. The carrier gas was methane, and the retention volume of the methane was measured by the use of radioactive methane. The detailed experimental results will be reported elsewhere.[7] The retention volume of helium perturbation is a first-order approximation of the gas-phase volume of the column packed with Porasil. Figure 2 gives the helium perturbation obtained by means of the apparatus equipped with the present flow meter in comparison with those obtained with a soap-film flow meter. If the density of the adsorbed methane is constant at a fixed temperature, the gas-phase volume decreases linearly with the methane adsorption.[3] The present flow meter improved the measurement very much. As may be seen in Table 1, the scattering is approximately 0.06%, at least 4 times better than in careful measurements by means of a soap-film flow meter.

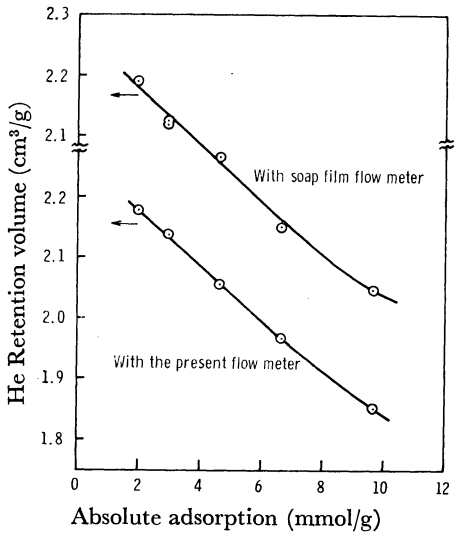


Fig. 2. Measurement of He retention volume by high pressure gas chromatographic apparatus equipped with and without differentiator.

Financial support was supplied by the U. S. National Science Foundation.

### References

1) J. F. Oberholtzer and L. B. Rogers, *Anal. Chem.*, **41**, 1234 (1969).
2) M. Goedert and G. Guiochon, *ibid.*, **42**, 962 (1970).
3) Y. Hori and R. Kobayashi, *J. Chem. Phys.*, **54**, 1226 (1971).
4) H. B. Gilmer and R. Kobayashi, *A. I. Ch. E. J.*, **11**, 702 (1965).
5) J. J. Haydel and R. Kobayashi, *Ind. Eng. Chem., Fundametal*, **6**, 546 (1967).
6) S. Masukawa and R. Kobayashi, *J. Gas Chromatogr. Sci.*, **6**, 257 (1968).
7) Y. Hori and R. Kobayashi, This Bulletin, to be published.