The output of the downstream detectors during a transient resulting from a step change was not pure sine waves. The outputs cannot be interpreted simply during the transient. Therefore the period of the sine wave generator must be less than the probable frequency of input sample composition changes.

The key to reducing the response time of the continuous gas chromatograph is to increase the sine wave generator frequency and proportionately reduce the column lengths. Carter (1964) suggests that by using 60-cycle-per-minute frequencies and columns about 0.8 inch long, the transient response could be reduced to about 4 seconds.

Reduction to Practice

The present continuous gas chromatograph is an experimental apparatus, designed to test the principle. To use it in monitoring a process stream, it would be necessary to provide a special-purpose computer to detect phase and compute composition automatically. This would replace reading the digital phasemeter visually and transferring the measurements to a general-purpose digital computer to calculate composition.

Probably the best way to compute composition automatically will be to make an analog device which automatically amplitude-modulates and then sums an externally generated electrical set of sine waves corresponding to the pure component sine waves to give a set of mixture sine waves that match the output sine waves of the detectors.

It will also probably be desirable to use input frequencies 10 to 20 times the input frequency of the prototype and to decrease column segments to 1/10 to 1/20 of their present length. This is expected to reduce the transient response to a step change in sample input from the present 30 to 40 seconds to 1.5 to 4 seconds. It would also simplify phase detection or comparison, because higher frequency electric signals are easier to work with.

The continuous gas chromatograph should be applicable to sample systems which have no more than six major components and which give measurably different phases with an attenuation factor, Θ_{jk}, greater than 0.2 in an isothermal chromatographic column. In its present form it is not suitable for assaying trace quantities. All components to be measured should be present at 5% concentration or more.

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Nomenclature

A_j = pseudomole fraction of jth component
C = pseudomolar concentration of n-component sample gas, gram-moles/cu cm
c_j = pseudomolar concentration of jth component, gram-moles/cu cm
t = time, sec
z_k = distance of kth downstream detector from column inlet, ft

Greek Letters
α_{jk} = phase of jth component sine wave at kth downstream detector relative to inlet, radians
Θ_{jk} = ratio of amplitude of jth component sine wave at kth downstream detector relative to its amplitude at inlet
Φ_k = phase of sum of pure component sine waves at kth downstream detector, radians
ω = angular velocity of piston movement

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Improvements to the Mercury-Seal Piston Flowmeter

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The mercury-seal piston flowmeter is particularly suitable for the measurement of low rates of gas flow (1 to 10^3 cm^3 sec^{-1}) with high accuracy and it may be used as a primary standard. This paper describes modifications to the basic piston flowmeter which reduce and even out the backpressure from the meter, permit continuous flow measurement, and provide a simple and easily adjusted electronic timing system.

The attainment of an accuracy better than ±1% in the measurement of gas flow, particularly at low flow rates (1 to 1000 cc per second), is by no means a simple task, although accuracies of ±0.2% are often claimed or implied, without much justification (Levy, 1964; Reed and Sprange, 1968).

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The accuracy of a given flowmetering system is dependent chiefly upon the accuracy of the primary or secondary standard with which it was calibrated. The meters most frequently used as primary or secondary standards are the rotary wet-seal meter and the soap-bubble meter (Levy, 1964). Both meters require saturation of the gas prior to its passage through the meter and the range of gases is limited to those that do not interact with the liquid in the flowmeter. The saturation of the gas being metered presents no difficulty at the lower end of the flow rate range considered here, but at the higher flow rates appreciable inaccuracies can arise (Levy, 1964), because of temperature changes during saturation of the gas. Also, the rotary wet-seal meter and the soap-bubble meter have a rather narrow range of volumetric flow rates over which accurate flow measurements may be made with a given size of meter. The range is about four to one in each case, although the range of the bubble meter can be extended considerably by the introduction of electronic timing, but there are appreciable difficulties in setting up such a timing system, chiefly due to variations in the optical characteristics of the bubble.

These, and other drawbacks of the rotary wet-seal and the bubble meter, are largely surmounted by the mercury-seal piston flowmeter (Porter, 1958).

This paper describes various modifications to the mercury-seal piston flowmeter which reduce and even out the backpressure from the meter, allow continuous flow measurement, and provide a simple, and readily adjusted, electronic timing system.

Basic Mercury-Seal Piston Flowmeter

The basic mercury-seal piston flowmeter developed by Porter is usually made up of a poly(vinyl chloride) piston, provided with what is effectively a mercury piston ring. The piston, sealed in this way, is located within a precision bore glass tube which can be calibrated. The mercury seal is established by forcing mercury, from a small reservoir at the axis of the piston, through a number of radial passage ways, into an annular groove cut in the cylindrical surface about midway up the piston wall. The complete piston flowmeter or the piston and tube only may be obtained from the Brooks Instrument Division, Emerson Electric Co., Hatfield, Pa., or from Brooks Instruments, Ltd., Stockport, England.

To try out the modifications with which this paper deals, a piston was made up, in the authors' workshops, to the dimensions shown in Figure 1. This piston was used in conjunction with a 1200-mm length of precision bore glass tube of 33 ± 0.01-mm internal diameter, supplied by Jencons, Ltd., Hemel Hempstead, Herts., England.

In the normal mode of operation, the gas to be metered is introduced to the underside of the piston and the time taken for the piston to pass between two precalibrated marks on the tube is measured. When the piston has passed the topmost fiducial mark on the tube, the gas supply to the underside of the piston must be vented so that the piston falls, under its own weight, to the base of the tube, in readiness for the next timed ascent. The backpressure on the flowmeter being calibrated or on the system, the flow through which is being measured, varies by an amount that depends on the weight of the piston and its cross-sectional area. The change in backpressure between the timing and venting run may be inconvenient, although it can be circumvented if a sufficient pressure is placed on the flowmeter to render the pressure difference insignificant, or if the vent line is restricted to give a backpressure that matches that due to the weight of the piston. However, in many situations such action is either not feasible or not convenient.

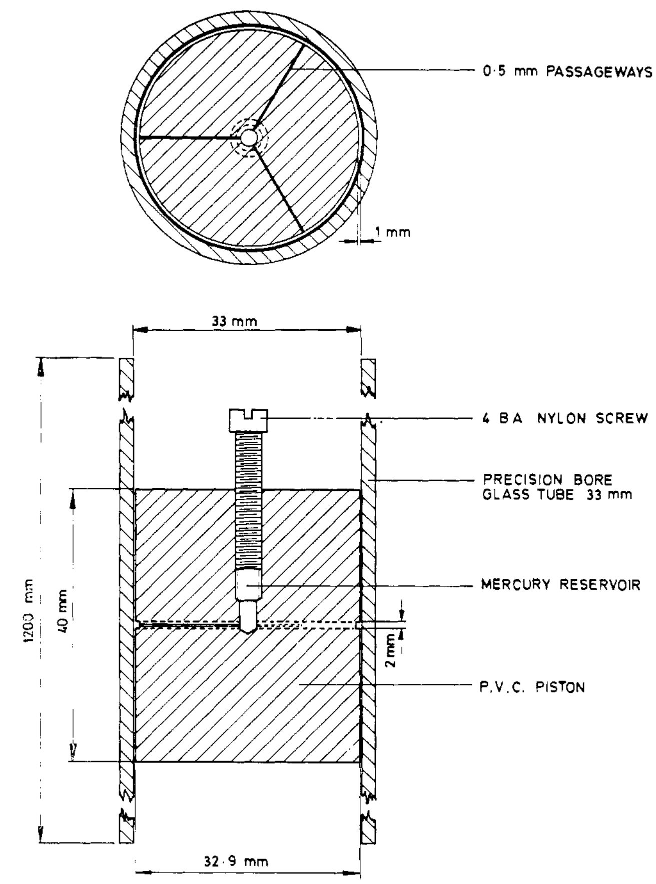

Figure 1. Details of piston-tube combination

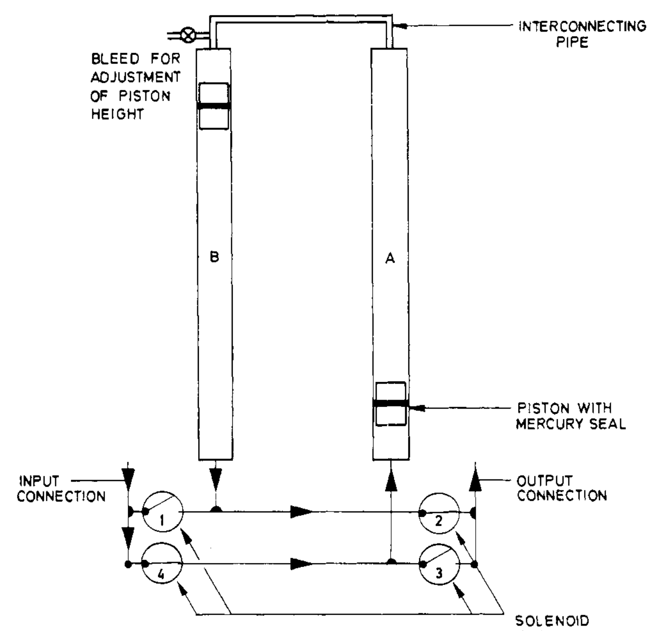

Figure 2. Twin-tube arrangement of mercury-seal piston flowmeter

Modification to Reduce and Even Out Backpressure

The difference in backpressure, exerted by the piston flowmeter during the timing and venting run, can be effectively eliminated by using a pair of piston and tube units and interconnecting the space above the piston in each unit, as shown in Figure 2. With this arrangement, the weight of the piston in one tube counterbalances the weight in the adjacent tube and the difference in backpressure between the timing and venting run is reduced from about 30-mm water gage to less than 3 mm. In addition, if the interconnecting tube is sufficiently large, the backpressure from the meter is reduced to only a few millimeters of water. An interconnecting tube with an internal diameter of 1.25 cm was used in the present case.

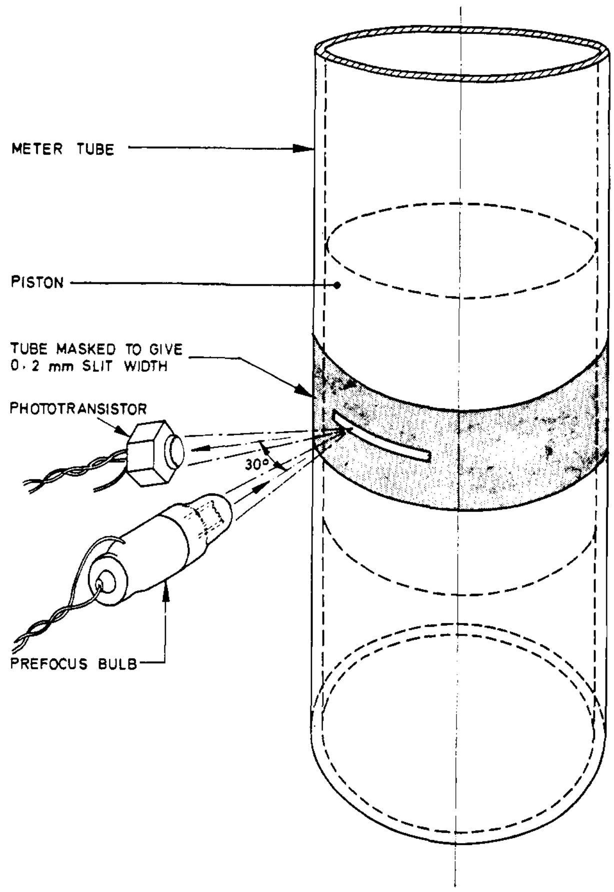

Figure 3. Optical arragement of piston sensing device

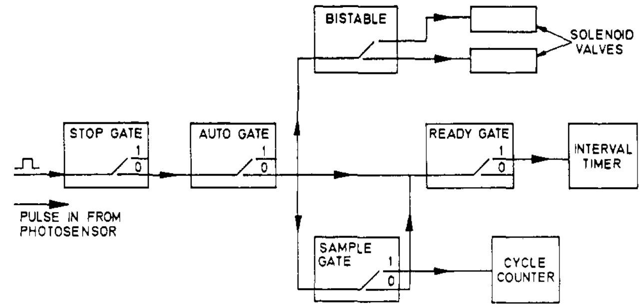

Figure 4. Simulated logic diagram for twin-tube piston meter modified to allow continuous flow and automatic control

Gates				
Stop	Auto	Sample	Ready	Operating Mode
1	0	0	0	Meter stopped, gas bypassed between inlet and outlet
0	0	0	0	Meter running in "one-shot" mode, timer disconnected
0	0	0	1	Meter running in "one-shot" mode, timer connected
0	1	0	0	Meter running in "continuous" mode, timer disconnected
0	1	0	1	Meter running in "continuous" mode, timer connected
0	1	1	1	Meter running in "continuous" mode, timer disconnected, counter connected

Modification for Continuous Flow Measurement

The paired-tube arrangement referred to above facilitates the modification of this type of flowmeter to permit continuous measurement of volumetric gas flows. This is achieved by means of four, twin-port, solenoid valves interconnected as shown in Figure 2. The solenoid valves may be switched so that gas is supplied first to the underside of the piston in tube A and then to the underside of the piston in tube B, and so on. To preserve the very low and uniform backpressure, associated with the twin-tube piston flowmeter, the solenoid valves must be large enough to give negligible backpressure and especially be matched so that the pressure drop across the solenoid valves is the same whatever the flow path. Matching to give equal pressure drops was found difficult if three-port valves were used.

Modification to Give Electronic Timing and Automatic Control

The piston may be sensed at any predetermined point along the tube, using the mercury seal as a mirror to reflect light from a prefocus bulb onto a phototransistor. To the authors' knowledge, this method was first proposed by Lindow (1966).

In the present instance, a prefocus torch bulb and a Mullard BPX25 phototransistor were mounted as shown in Figure 3. The bulb and phototransistor were located 4 and 3 mm from the tube surface, respectively, but these distances were not critical. This unit was then clipped on one of the pair of piston-tube units opposite one of a number of horizontal slits 0.2 mm wide, formed by local masking of the tube. A similar sensor was located some distance along the tube, so as to give a convenient timing interval. In the instrument developed by the authors, sensing slits were located to allow displacements of the piston of approximately 200 and 750 cc to be timed.

The sensing arrangement in which the mercury seal on the piston is used as a mirror was much easier to set up than the system commonly used in similar situations, in which the piston (or soap bubble, or mercury pellet) interrupts a beam of light shining diametrically across the tube (Bailey *et al.*, 1968). The reflection system contains fewer parts and gives an output signal that is more suitable for triggering than that given by an obscuring system.

Successive output pulses from the reflection-type sensors described above can be used to actuate an electronic or electromechanical timer, depending on the accuracy required, and to control the operation of the solenoid valves used to switch the flow between one tube and the other. In the present instance, provision was made for choosing one of a number of operating modes. The simulated logic diagram of the arrangement used and the possible operating modes are shown in Figure 4.

Calibration of Modified Piston Meter

Static Calibration. The volume swept out by the piston, between the various fiducial marks, was calibrated by water displacement and subsequent weighing. The piston sensors were in position during calibration and the actuation of the timer in the sensor circuit was taken as the point at which the piston had reached a given fiducial mark. When carrying out this measurement of the volume swept out between fiducial marks, the piston approached both the upper and lower fiducial mark from below. Thus, both the upper and lower sensors were triggered by light reflected from the top edge of the mercury seal. This gives the volume to be used when operating in the "one-shot" mode. In the continuous mode, the upper sensor is triggered by the top edge of the mercury seal, but the lower sensor is triggered by the bottom edge. Determination of the volume swept out by the piston in moving from the top-edge to the bottom-edge triggering position, on the same fiducial mark, gave a value of 2.26 cc. When the meter was used in the continuous mode, this volume was subtracted from the volume between any two fiducial marks, as determined by static calibration, to obtain the volume swept out by each traverse of the piston in the continuous mode.

The accuracy of the static calibration of volume was estimated to be about $\pm 0.05\%$ for the 200-cc volume and $\pm 0.02\%$ for the 750-cc volume. In addition to these possible errors, errors may be incurred in the measurement of the pressure and temperature of the gas within the flowmeter and in the measurement of the time taken for the piston to traverse between any two fiducial marks. With reasonable care, the error in measuring pressure and temperature should not be greater than $\pm 0.05\%$ in each case and, if an electronic timer is used, the timing error should not be greater than $\pm 0.01\%$ for timing periods greater than about 5 seconds.

Thus, the random error, when the meter is operating in the "one-shot" mode, should not be greater than $\pm 0.16\%$.

In the continuous mode, further errors may arise as a result of gas bypassing the flowmeter during the switchover of the solenoid valves and piston overtravel at high flow rates. To establish whether there are additional errors, the operation of the meter in the continuous mode was investigated.

Dynamic Calibration. The dynamic calibration was carried out using a meter-prover, which consisted of an arrangement whereby a controlled flow of compressed air forces water from a reservoir into a cylinder. The air displaced from the latter passes into an auxiliary cylinder and the air in this, which is of relatively low humidity, passes through the meter being calibrated. In this way a volume of approximately 51 liters (to the nearest complete traverse of the piston) was passed through the twin-tube piston meter; the exact volume was determined from the reading on the sight glass of the meter-prover. This procedure was carried out for a range of flow rates up to 300 liters per hour, with the piston sensors set to allow the piston to sweep out approximately 750 cc between each traverse. The correspondence between the total volume flow indicated by the piston meter and that indicated by the prover varied, without showing any consistent trend, as the piston speed increased with increase in the flow rate, but the difference was always less than $\pm 0.6\%$. A further series of tests was then carried out with the upper sensor located at the 200-cc fiducial mark. With the sensor in this position, the number of switchovers of the solenoid valves and changes in direction of the piston is about 3.7 times greater, for the passage of a given volume, than when the sensor is at the 750-cc fiducial mark. The results of this series of tests showed that the total volume passed, as indicated by the piston meter, did not differ by more than $\pm 0.6\%$ from that indicated by the prover, up to a flow rate of 100 liters per hour. Above this flow rate, the piston flowmeter consistently indicated a lower total flow than the prover and the discrepancy increased rapidly with increase in flow rate above 100 liters per hour. This indicates that gas was bypassing the piston meter during the change-over period of the solenoid valves.

Conclusions

The twin-tube mercury-seal piston flowmeter provides one-shot flow measurement to an accuracy better than $\pm 0.16\%$ and continuous flow measurement to $\pm 0.6\%$.

The flow rate range is from 4 to 300 liters per hour, the lower limit based on the assumption that timing intervals greater than 3 minutes would not generally be convenient. This range could be extended by increasing or decreasing the size of the piston and tube combination.

The gas need not be saturated prior to its passage through the flowmeter and the few restrictions on the nature of the gas can be dealt with.

Pressure drop across the flowmeter is insignificant.

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