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THEORETICAL AND EXPERIMENTAL OPERATING CHARACTERISTICS OF A PNEUMATIC GAS CHROMATOGRAPHIC DETECTOR

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SUMMARY

The operation of an orifice–capillary combination as a detector for gas chromatography is examined in detail. Experimental results are compared to those predicted from a computer model of the system.

INTRODUCTION

A totally pneumatic based process control chromatograph and signal processor has been presented in the recent literature[1,2]. The purpose of that initial publication was to describe the development of the entire system consisting of a viable pneumatic detector, thermostated steam heated enclosure and a programming technique which allowed the automation of the unit using standard pneumatic components. Because of space restraints, it was not possible in a paper of such broad coverage to treat any one topic at great length.

The purpose of the present report is to examine in greater detail the operation and performance of the pneumatic detector used in the system.

INTRODUCTORY THEORY

The detection system employed a 0.002 in. diameter orifice in series with a capillary tube to generate pressure signals as sample components emerged from the column and passed through the detector. The small differential pressure signals were amplified by an amplifier as shown in Fig. 1, so that the final signal was in the 3–15 p.s.i. range.

The flapper nozzle unit, amplifier relay and feedback bellows of Fig. 1 are arranged in a force balance system. Any difference between orifice and capillary pressure is sensed by movement of the flapper from its equilibrium position at the nozzle. This in turn is reflected as a change in the output signal of the relay which is also fed to the feedback bellows. The magnitude of this feedback signal is sufficient to keep the flapper at its equilibrium position and thus is proportional to the disturbing force. Gain is achieved through the area relationships and positions of the bellows with respect to the pivot point of the lever arm. The output range of the relay is usually 3–15 p.s.i.

The capillary signal was used to compensate for that portion of the orifice

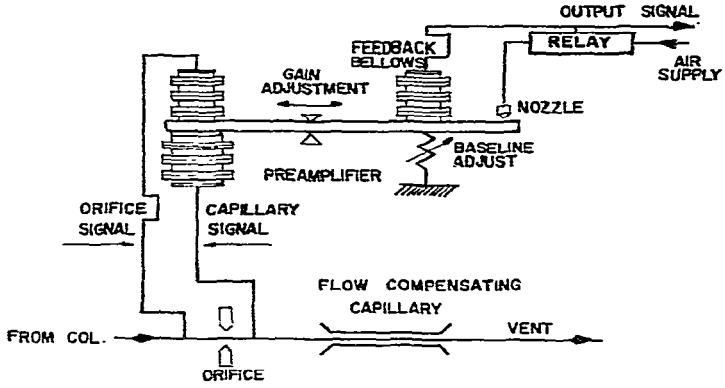


Fig. 1. Orifice–capillary detector and force-balance pneumatic amplifier.

signal which was flow dependent. However, as will be shown further along it also increased peak sharpness, thus enhancing resolution.

The chromatographic signal produced by this detection system can be shown to be the result of differences in density and viscosity between carrier gas and sample components.

The pressure drop ΔP_o across an orifice can be shown to be

$$\Delta P_o = K_o \varrho F^2 \tag{1}$$

where K_o is a constant, ϱ the density of the gas in the orifice, and F the flow-rate of the gas.
The signal due to a component results from a density change, $\delta\varrho$,

$$\frac{\delta \Delta P_o}{\delta \varrho} = K_o F^2 \tag{2}$$

whereas a flow change, δF, gives a signal

$$\frac{\delta \Delta P_o}{\delta F} = 2 K_o \varrho F \tag{3}$$

In the case of a capillary tube the pressure drop ΔP_c is a function of viscosity η and flow

$$\Delta P_c = K_c \eta F \tag{4}$$

where K_c is a constant.
A flow change, δF, also gives a signal

$$\frac{\delta \Delta P_c}{\delta F} = K_c \eta \tag{5}$$

By amplifying the two pressure signals at appropriate gains A_o and A_c so that

$$2 A_o K_o F = A_c K_c \eta \tag{6}$$

and subtracting

$$2 A_o K_o \varrho F - A_c K_c \eta = 0 \tag{7}$$

We can eliminate flow as a variable leaving the detector response to a component as

$$\delta P_{out} = A_o K_o F^2 \delta\varrho - A_c K_c F \delta\eta \tag{8}$$

Using helium as a carrier gas, the density change, $\delta\varrho$, is positive while the viscosity change, $\delta\eta$, for most sample components is negative. Thus, the detector output becomes the sum of these two terms.

Hydrogen produces a positive signal because the negative viscosity difference is much larger than the negative density difference (see Fig. 13). The sensitivity of the detector for the measurement of hydrogen is therefore expected to be much less than for a hydrocarbon. The computer model predicts that the detector signal for hydrogen will be about 10% of that for ethane if both peaks elute at the same time (see Fig. 9).

In practice with the experimental set-up used in this research the normalized hydrogen peak height response was about 9% of that for ethane. There are other consequences of this large viscosity difference which will be discussed in the section concerned with the analysis of hydrogen.

With hydrogen as carrier gas the viscosity differences are smaller and may be negative or positive depending on the sample component. However, the final signal is still positive due to the large positive density changes.

EXPERIMENTAL

All experimental work reported herein was obtained using a commercially available pneumatic chromatograph (Model 91PCT, The Foxboro Co., Foxboro, Mass., U.S.A.). The unit was operated in a single column configuration (6 ft. × 3/16 in. O.D., 30% ethoxy-ethyl sebacate on 80–100 Chromosorb P) at ambient temperatures and was equipped with a 1-ml sample loop.

Samples were prepared in 500 in.^{3} low pressure (100 p.s.i.g.) tanks fitted with dial type Weston thermometers. Previously calibrated 6-in. bourdon tube gauges (readable to 0.5 p.s.i.g.) were used to measure the partial pressure of each added gas. The accuracy of this sample preparation technique was established by analyzing a certified analytical gas sample prepared by Air Products and Chemicals (Tamaqua, Pa., U.S.A.). On the basis of these results it was established that samples prepared in these laboratories were accurate to better than 1% relative.

In order to document the experiments described in this report, it was necessary to record chromatographs. Since a pneumatic recorder was not available, it was necessary to transduce the pressure signals to voltage (ICT Model 6000, 0–20 p.s.i. transducers) before presentation to a mV recorder. The ordinate of all figures is labeled as pressure which is the original detector quantity.

Modeling was done on a Data General Supernova minicomputer with 8K of core. The Extended Basic which was used was modified with assembly language subroutines to drive an Hewlett-Packard 7045A high-speed X–Y plotter through a pair of Datal 10 bit D/A converters.

VISCOSITY–CONCENTRATION RELATIONSHIPS

Since detector response is related to the difference in both viscosity and density of the carrier gas and the component of interest, these properties must be linearly related to concentration for the detector to respond linearly. The equations of Wilke[3], however, indicate that the viscosity–concentration relationship is not linear over the total range of concentrations. Plots of viscosity *vs.* concentration over the range 0–1% using Wilke's equations are shown in Fig. 2 for hydrogen, methane, ethane, propane, butane, and isobutane. Ranges larger than this begin to show significant deviations in linearity. It is possible that an injection of a 1-ml sample containing a large concentration of an early eluting component might yield a detector concentration surpassing this limit. However, it is expected that chromatographic non-linearities will become limiting long before reaching the viscosity limit[1]. Thus, it is recommended that smaller sample loops (200 μl) be used for the analysis of samples in the 50–100% range.

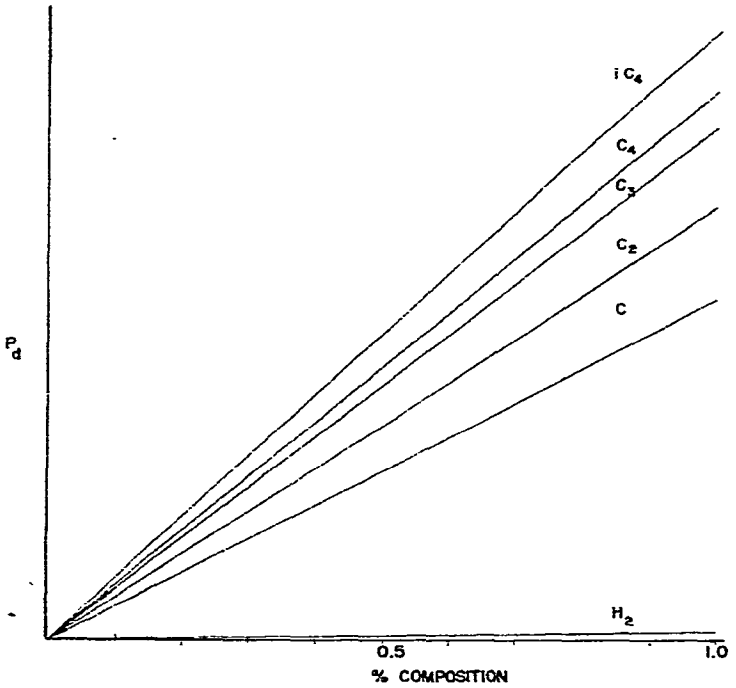


Fig. 2. Computer plots of theoretical detector output *vs.* percent composition of hydrocarbon or hydrogen in helium. Wilke's eqns.[3] were used to calculate viscosity at each composition and a linear density–concentration relationship was assumed. C = methane; C_2 = ethane; C_3 = propane; C_4 = butane; iC_4 = isobutane.

DETECTOR GEOMETRY

The detector output described by eqn. 8 will be linear only if flow is held constant. The assumption that no local flow perturbations occur as sample traverses the detector may not be valid. Capacitor volumes are closely coupled to the orifice input (measurement bellows and connecting tubing) which can act as low impedance flow reservoirs or flow sources when the sample component reaches the orifice and causes sudden pressure changes to occur. It was thought that this increased pressure as a driving force to fill side volumes might make these post column dead volumes a more serious problem than reported by Maynard and Grushka[4] for other detectors. However, as will be shown experimentally and through simulation the post-column volumes are not important peak degradation mechanisms for the orifice–capillary detector system.

The other aspect of the problem, that of non-linear peak height *vs.* concentration relationships due to flow changes during peak passage through the detector, also does not appear to be of great importance. Linear behavior was originally reported to 10% concentration of component[1] but has been observed to 70% and higher using smaller sample volumes[5].

COMPUTER MODEL

A very simple model of the system was conceptualized and written in Basic. The fundamental equation used to characterize the system is shown below.

$$P_{in} = \eta_{col} K_{col} F + \varrho_{or} K_{or} F^2 + \eta_{cap} K_{cap} F \tag{9}$$

where P_{in} is the pressure at column inlet, η_{col}, η_{cap} are the viscosities of the gas in column and capillary, respectively, ϱ is the density of the gas in the orifice, K_{col}, K_{or}, K_{cap} are the constants for column, orifice, and capillary determined experimentally, and F is the flow-rate.

Compressibility corrections were not made and the model did not contain any chromatographic equations. The sample was introduced as a 100-volume sliced peak of appropriate shape and it traveled through the system undisturbed except from flow perturbations caused by density or viscosity differences. New values of pressure and flow were calculated as each volume slice reached a new position in the system.

The orifice was assumed to accommodate one volume slice. The capillary could be positioned close to the orifice to simulate a small dead volume between them. Thus, a volume slice exiting the orifice could enter the capillary directly. Also, the volume of the capillary could be continuously varied so that it could be filled with one volume slice or the total peak. This latter option constituted an attempt to model the possible situation presented by early eluting peaks and fast columns. Indeed, the computer generated signal for this option looks remarkably similar to that observed experimentally for fast eluting peaks (see Fig. 3). However, detector response characteristics (mechanical overshoot) were not ruled out as also contributing to this phenomena.

The model provides a simple picture of detector–peak interaction. Consider the situation where a capillary is not being used and a portion of the peak is in the orifice. The pressure has increased at the orifice since density has increased. If a low

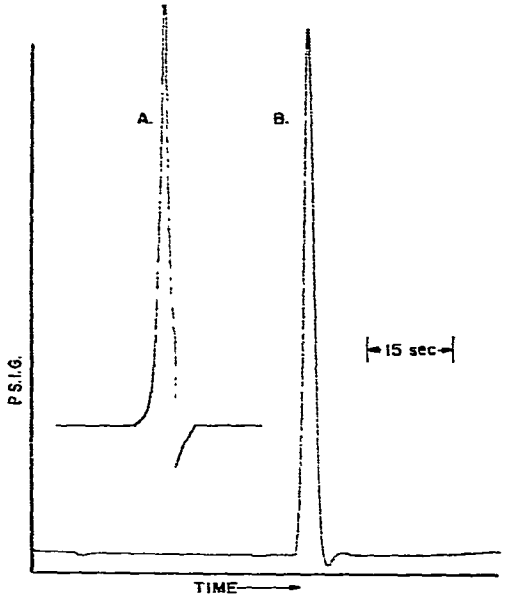


Fig. 3. Anomalous peak shapes. A, computer model output assuming that some portion of the sample has a finite residence time in the capillary after all of the sample has passed through the orifice; B, experimental chromatogram of 5% methane–helium sample obtained at a helium flow-rate of 60 ml/min.

resistance connection to the flow source were available, flow would change as the pressure controller tried to maintain P_{in} constant. However, this action is time-delayed by the high resistance of the column. This assumption is translated into the model by assuming the first term in eqn. 9 is constant.

Thus, flow into the orifice is diverted so that low impedance side volumes (such as connecting tubing and measuring bellows) are filled to the point where their pressure is equal to that at the orifice. This process reverses itself when the maximum

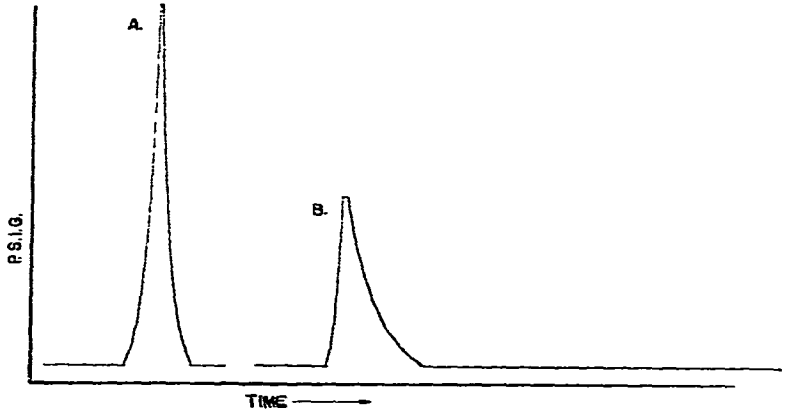


Fig. 4. Computer model output using only an orifice as a detector. A, no side volumes; B, 20 ml side volume before the orifice.

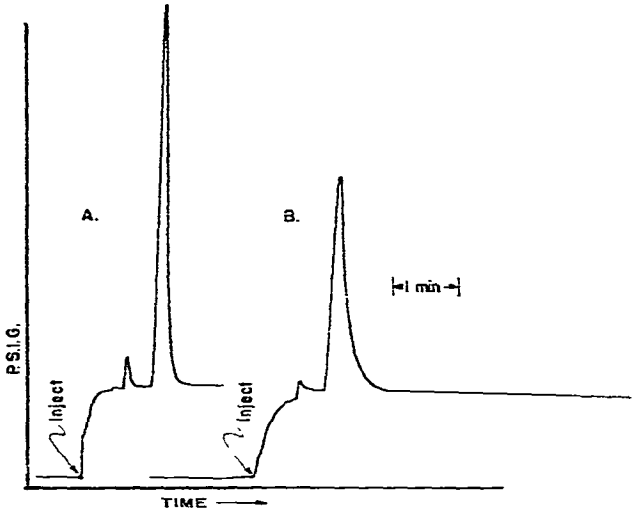


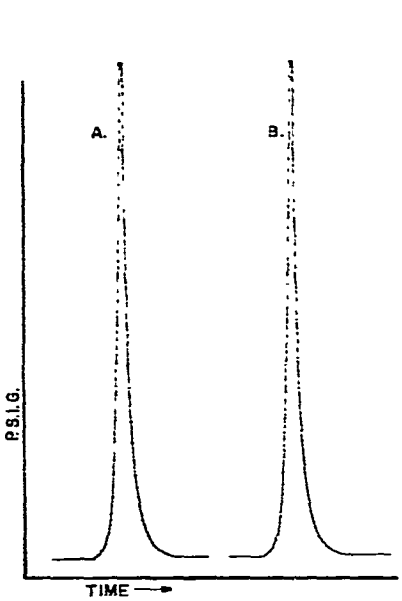
Fig. 5. Chromatograms of propane obtained in the laboratory using only the orifice as a detector. The constant baseline offset which occurs after injection is caused by the decreased resistance to flow which occurs when the sample valve is in the inject position. A, the only side volume present is that of connecting tubing and measurement bellows; B, an extra 15-ml side volume has been connected to the input at the orifice.

of the peak has passed through the orifice. The total effect is to reduce the peak height, and shift slightly the peak maximum. If the side volumes are large so that appreciable mixing of the sample and carrier gas occurs considerable peak tailing occurs. Examples of computer generated detector outputs illustrating these cases are shown in Fig. 4. They are quite similar to experimentally produced chromatograms using only an orifice and large added side volumes to demonstrate these phenomena (see Fig. 5).

In the presence of the capillary the situation is quite different. Consider the same problem as above except that now a portion of the peak is also in the capillary as well as the orifice. The pressure at the capillary is now decreased because the viscosity of the gas in the capillary has decreased (compared to carrier gas). Thus, the pressure drop across the orifice is larger when a capillary is present than when it is absent. This added pressure drop provides an extra driving force for increased flow through the orifice, thus decreasing side volume flow and increasing detector sensitivity.

Computer plots of an orifice–capillary detector system with and without the large side volume previously used in the orifice-only experiments are shown in Fig. 6. The same conditions reproduced in the laboratory yielded the chromatograms shown in Fig. 7. Again, the correspondence is quite good.

The action of the capillary as modeled above is not immediately obvious. Interestingly, the capillary emerges as something more than a flow compensator. It provides a derivative action to the tailing edge of the peak. The magnitude of this effect depends in general on a relationship of peak volume, capillary volume and viscosity differences. It may be fairly large and easily recognizable as shown in Fig. 3 or the origin of the small but significant contribution to resolution illustrated in Fig. 8.



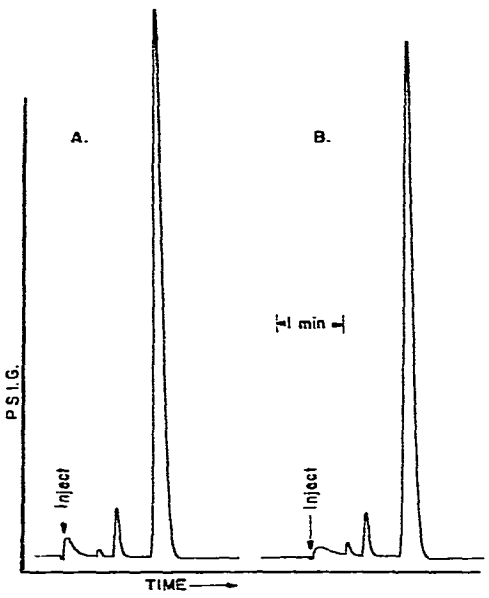


Fig. 6. Computer model output using an orifice–capillary detector. A, no side volumes; B, 20 ml ide volume connected before the orifice.

Fig. 7. Chromatograms of propane obtained in the laboratory using the orifice–capillary detector. A, only connecting tubing and measurement bellows present as a side volume; B, an extra 15-ml side volume was connected to the input at the orifice.

Thus, the experimental observation concerning the relative unimportance of post column side volumes is also not surprising.

A computer constructed graph of peak height *vs.* concentration using this model is shown in Fig. 9. It shows minimum curvature of the 0–1% range, the most

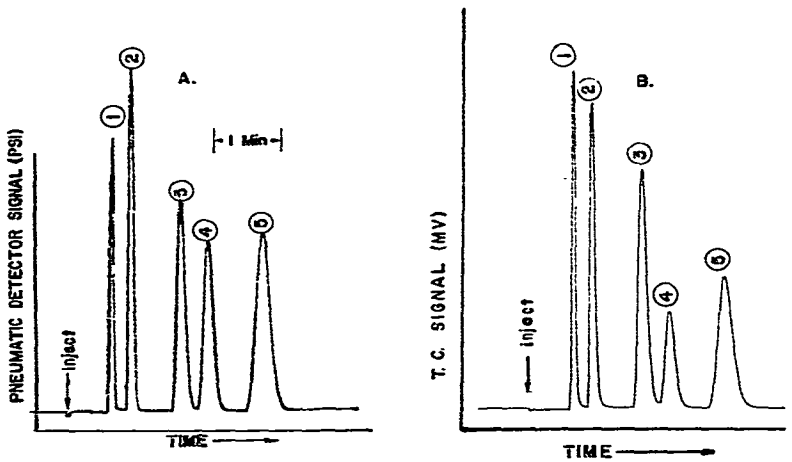


Fig. 8. Comparison chromatograms obtained of a hydrocarbon sample using the pneumatic chromatograph (A) with the pneumatic detector and (B) after substituting a 25-μl volume thermal conductivity cell for the pneumatic detector. Compare the resolution between propane and propylene. 1 = Methane, 2 = ethane, 3 = propane, 4 = propylene, 5 = isobutane.

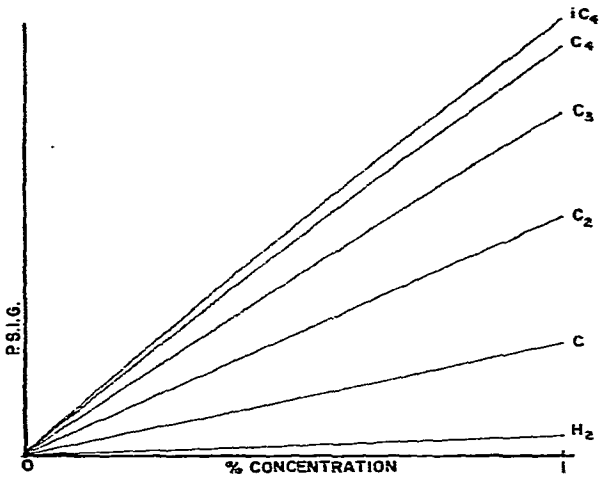


Fig. 9. Peak height–concentration output from the computer model.

likely detector sample concentration range. It should be noted that all peaks appear at the same retention time and retain the same peak shape as when injected. Thus, they do not show the influence of chromatographic retention mechanisms on peak height. Therefore, the predicted relative sensitivities will not be observed experimentally. It is obvious, however, that higher molecular weight longer retained peaks will have a higher relative signal than found when using a detector which responds to some general property like thermal conductivity.

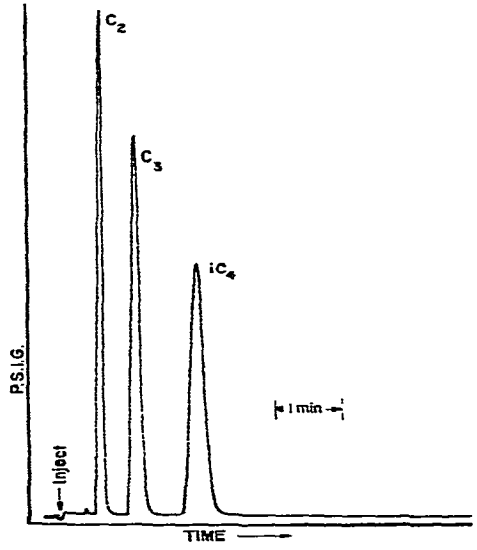


Fig. 10. Chromatogram of a hydrocarbon mix with helium as carrier gas.

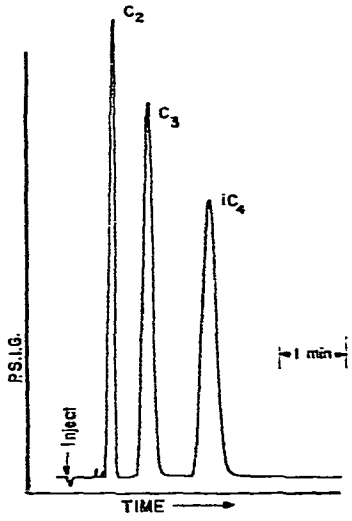


Fig. 11. Chromatogram of the same hydrocarbon as shown in Fig. 10 but using hydrogen as carrier gas.

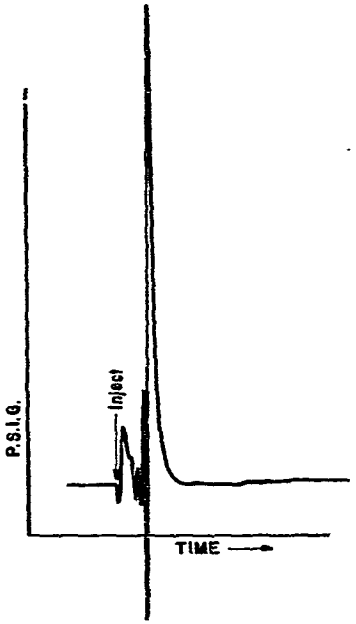
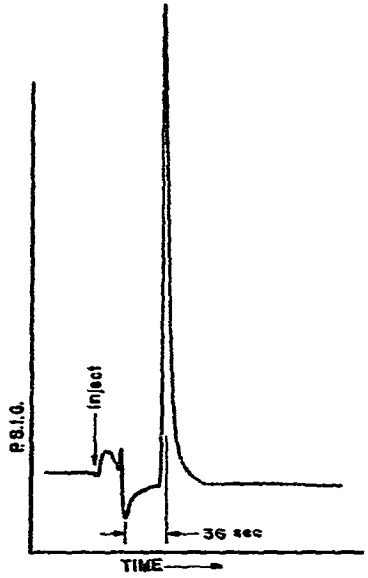


Fig. 12. Chromatogram of hydrogen obtained on the unmodified system using helium as carrier gas.



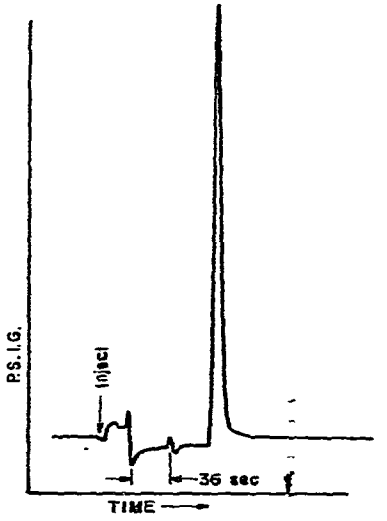


Fig. 13. Chromatogram of hydrogen obtained under the same conditions as that of Fig. 12 except that 8 ft. × 3/16 in. O.D. tubing has been added between the column exit and the detector input. The residence time of hydrogen in this added 8 ft. of tubing at the flow-rate of 58.3 ml/min was found to be 36 sec.

Fig. 14. Chromatogram of hydrogen illustrating the isolation of pressure disturbances. The chromatogram was obtained under the same conditions as that of Fig. 13 except that a capillary restrictor was placed at the end of the first delay line and this was followed by another nominally 8 ft. × 3/16 in. delay line connection to the detector.

HYDROGEN CARRIER GAS

No significant differences in performance of the detector were found when using hydrogen rather than helium as a carrier gas. Chromatograms of the same mixture with helium and hydrogen carrier gases are shown in Figs. 10 and 11.

ANALYSIS OF HYDROGEN

Since the pneumatic chromatograph can be used in hazardous areas, one obvious application is the analysis of hydrogen rich samples (*e.g.*, reformer gas). Preliminary experiments yielded unacceptable chromatograms (see Fig. 12) with baseline perturbations appearing before the emergence of hydrogen and thus interfering with its measurement. Moreover, the pattern of baseline disturbances appeared to depend on the particular column configurations which were used in the unit.

The problem was finally identified with the large negative viscosity difference between hydrogen and the helium carrier gas. As the hydrogen sample plug passed through large resistances (*e.g.*, 1/16-in. connecting tubing) there was a sudden pressure change which was transmitted down-stream to the detector. Various baseline patterns could be obtained by connecting resistances and delay lines at various places upstream of the detector (see Figs. 13 and 14).

The final solution involved connecting a delay line (8 ft. of 3/16 in. O.D. empty tubing) between the separation column and the detector. This delayed the hydrogen sufficiently so that pressure perturbations had subsided and a good sample of the baseline could be obtained before hydrogen was to be measured (see Fig. 15).

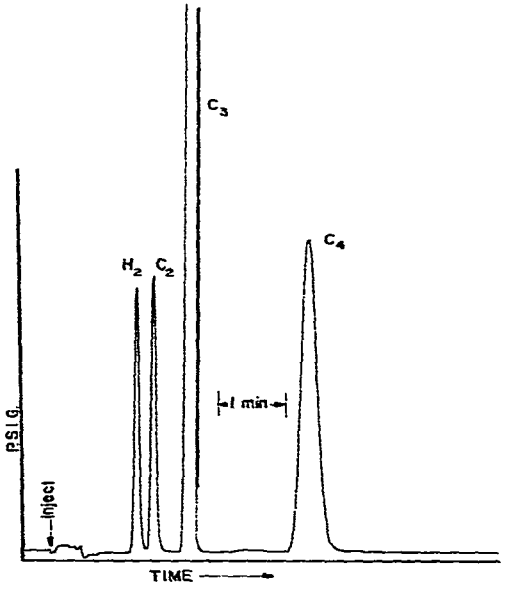
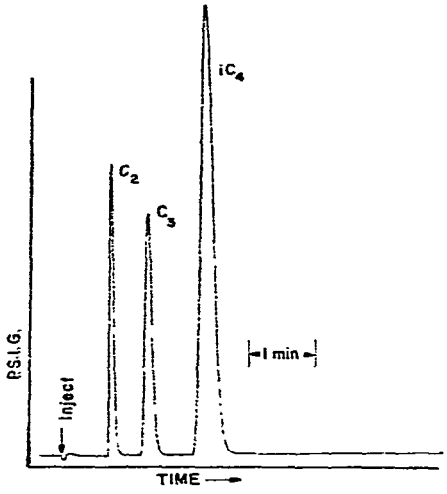


Fig. 15. Chromatogram of a sample containing 50% hydrogen, 5% ethane, 35% propane, and 10% butane. Carrier gas, helium. 8 ft. × 3/16 in. tubing added to column as a delay line.



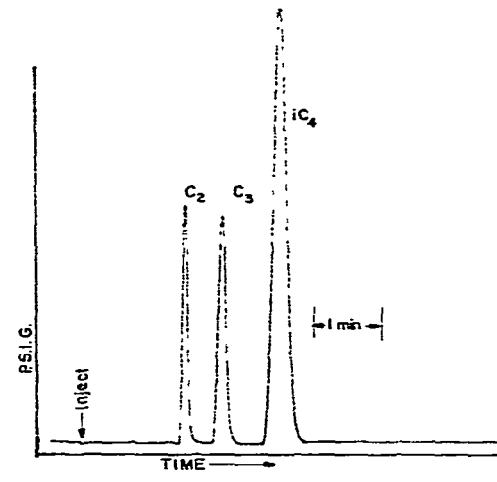


Fig. 16. Chromatogram of a hydrocarbon mixture without the 8-ft. delay line added to the system.

Fig. 17. Chromatogram of the same hydrocarbon mixture as shown in Fig. 16 with added 8-ft. delay in the system.

The addition of the delay line did not significantly affect resolution. Chromatograms of ethane, propane, and isobutane without and with the added 8-ft. delay line are shown in Figs. 16 and 17.

FLOW SENSITIVITY AND COMPENSATION

It is obvious that the flow compensation system shown in Fig. 1 maintains the baseline at its set point value when flow-rate changes. It does not maintain a constant sensitivity of the detector. That is, although much of the present research was conducted at helium flow-rates of 40–60 ml/min, the sensitivity of the detector can be increased by operating at higher flows. This mode of operation is particularly attrac-

TABLE I

ANALYSIS OF PROPANE IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF ISOBUTANE

Propane (%)		*Isobutane (%)*
Actual	*Measured**	
14.05	14.0	15.68
10.09	10.2	39.41
6.25	6.3	62.48
3.28	3.42	80.32
1.58	1.60	90.50
0.773	0.79	95.36
0.37	0.39	97.78

* Based on a calibration curve prepared from helium–propane mixtures.

tive when using hydrogen as a carrier gas since this low viscosity gas allows one to achieve the higher flow-rates at reasonable column pressures.

The flow sensitivity of the detector partially compensates for changes in peak height which occur with changes in temperature. Thus, as discussed previously[1] the detector is less sensitive to changes in the temperature of the column oven than other detectors.

Another aspect of this flow sensitivity which was not reported at that time was the possible sensitivity of calibration curves to sample composition. This effect which is operative in all chromatographic systems has been examined in great detail by Dyson and Littlewood[6]. As can be seen from the results shown in Table I, this effect is probably unimportant for analysis accuracies of 2–3%. Only at very large concentrations of the longer retained component or components will significant enhancement of the early eluting peaks take place. The method of calibration therefore will depend on the sample composition and the desired analysis accuracy.

CONCLUSIONS

The theoretical basis for the operation of an orifice–capillary gas chromatography detector has been presented and predicted performance characteristics have been verified by experiment. The detector behaves linearly as long as detector concentrations are kept in the range of 0–1%. Both hydrogen and helium have been found to make suitable carrier gases. The analysis of hydrogen is accomplished using helium as a carrier gas where hydrogen yields a positive peak at all concentrations examined.

The detector system produces chromatograms of at least equal resolution to those obtained using small volume thermal conductivity detectors and with peak heights whose sensitivity to variations in column temperature is less than that found with the latter detector.

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