TOTALLY PNEUMATIC GAS CHROMATOGRAPHIC PROCESS STREAM ANALYZER

RAYMOND ANNINO

Canisius College, Buffalo, N.Y. (U.S.A.)

and

JOHN CURREN, Jr., RICHARD KALINOWISKI, EDWIN KARAS, ROY LINDQUIST and ROBERT PRESCOTT

The Foxboro Company, Foxboro, Mass. (U.S.A.)

SUMMARY

A nonelectric pneumatic based process stream gas chromatographic analyzer is described. The unit automatically and repetitively analyzes a process stream for one or two preselected components and transmits a 3–15 p.s.i. signal which is proportional to their concentration in the process stream.

INTRODUCTION

A closed-loop process control chromatograph operates continuously, on-line, analyzing a process stream in a cyclic and repetitive manner. It transmits the information to a controller which then takes corrective action so as to maintain the process at the desired set point.

The factors, therefore, which determine the design criteria for this type of analyzer are quite different from those which influence the design of laboratory units[1]. For instance, the requirement for long-term stability and minimum down time over extended periods of unattended operation puts a premium on simplicity of design, ruggedness, and dependability of all components. The fact that the unit will usually be located in areas where hazardous concentrations of inflammable gases are present further complicates the design problem. On the other hand, many common process applications do not require low detection limits and thus the more exotic but trouble-plagued chromatographic detectors need not be used. In addition, programming the analysis cycle is simplified since control of the process can normally be achieved by monitoring only one or two components of the process stream.

Pneumatic process control instrumentation has a long history of proven reliability, serviceability, and safety, which is difficult to match. It was felt, therefore, that the development of a totally pneumatic chromatograph would be an excellent way to achieve the above stated objectives.

The purpose of this paper is to describe the development of a viable pneumatic detector, an appropriate thermostated steam heated enclosure, and a unique pro-

gramming philosophy which allowed the automation of the unit using standard pneumatic components.

ORIFICE DETECTOR

Theory
       The chromatographic detector which is to be described utilizes a jeweled orifice nominally 0.002 in. in diameter. This element responds to the density of the flowing gas by accelerating the gas to a higher velocity. The force required to produce this acceleration is measured as a pressure drop across the orifice and this constitutes the chromatographic signal. The theoretical pressure drop across the detector orifice is given by:

$$P_b = \frac{3 \, F^2}{K^2 \pi^2 \, d^4} \, \varrho \tag{1}$$

where
       F = volumetric flow-rate
       ϱ = density of gas within the detector
       d = orifice diameter
       K = orifice contraction coefficient (usually 0.62).
       In actual practice the exponent of F may vary depending on the ratio of internal length of the orifice to orifice diameter.
       Eqn. 1 can be used to calculate the orifice pressure due to carrier gas flowing at a specified rate and at a given temperature. For example, using an orifice of 0.0022 in. diameter and helium carrier gas at a flow-rate of 50 ml/min, orifice pressure is calculated to be 3.4 p.s.i., which is in good agreement with that obtained by experiment.
       The chromatographic signal may be visualized as appearing on top of this steady state signal. When helium is used as the carrier gas, the sample components eluting from the column are usually more dense than helium and ϱ increases, causing a proportionate increase in P_b.
       The total mass, m, of a sample component is assumed to be added to the carrier gas stream as a Gaussian distribution of concentration with time. It may be more conveniently viewed as a mass of sample distributed in a volume of carrier gas such that the increased density is a Gaussian distribution. The maximum increase in density can be shown[2] to be

$$\Delta \varrho_{max.} = \frac{m \sqrt{N}}{\sqrt{2\pi} \, V_r} \tag{2}$$

where N is the number of theoretical plates and V_r is retention volume. Since m is the product of (sample volume, V_s, concentration in the sample, C_c, and density of pure component, ϱ_s), at sampling pressure and temperature, then

$$\Delta \varrho_{max.} = \frac{V_s \, C_c \, \varrho_s \, \sqrt{N}}{\sqrt{2\pi} \, V_r} \tag{3}$$

Substituting for ϱ in eqn. 1 yields a pressure change in response to the density change of the eluting peak

$$\text{Peak height} = \Delta P_{\text{max.}} = \frac{8F^2 \Delta\varrho_{\text{max.}}}{K^2 \pi^2 d^4} \tag{4}$$

which becomes

$$\text{Peak height} = \Delta P_{\text{max.}} = \frac{8F^2 V_s C_c \varrho_s \sqrt{N}}{K^2 \pi^2 d^4 \sqrt{2\pi} V_r} \tag{5}$$

As can be seen in the equation the pressure drop is critically dependent on orifice diameter. It was decided early in the research that a sensitivity specification which would indicate a full-scale response for a 1-ml sample volume containing 1 % methane was a reasonable goal. In view of the limited gain of pneumatic amplifiers this specification required a 0.08 p.s.i. orifice pressure change at the methane peak maximum. Again the 0.002-in. orifice operated between 50–60 ml/min satisfies this requirement.

Flow sensitivity

The use of an orifice or capillary restrictor as a detector was first suggested by Griffiths et al.[3]. The main disadvantage of this detector for laboratory applications is its high sensitivity to flow variations.

The flow sensitivity of the orifice detector can be easily verified with eqn. 1. The baseline offset which results from slow changes in flow due to overall changes in system components such as regulators, etc., can be easily offset by splitting the carrier gas stream ahead of the column, passing this stream through a balancing restrictor and thence to another orifice, and taking the chromatographic signal as the difference in the two orifice signals. This is similar in philosophy to the thermal conductivity measurement system, and is the basis of a recent patent[4]. Unfortunately, no report is available in the open literature as to its performance. In any case it is doubtful whether this arrangement will compensate for the flow variations which occur due to viscosity changes in the flowing medium when it is mixed in the column with sample[*]. This effect and its implications for quantitative analysis have been discussed in detail by Dyson and Littlewood[6] and need not be elaborated here.

Fig. 1 is an amplified orifice detector signal obtained using the split stream design discussed above. The large offset in the baseline is due to the viscosity-modified flow which occurs while the sample is in the column; the baseline returns to its original value when the last peak elutes.

Flow compensation

The pressure drop across a capillary restriction is given by

$$\Delta P_{\text{cap}} = \frac{K F L \eta}{r^4} \tag{6}$$

---

[*] For a review of the various flow and pressure effects which accompany the elution of solutes, see ref. 5.
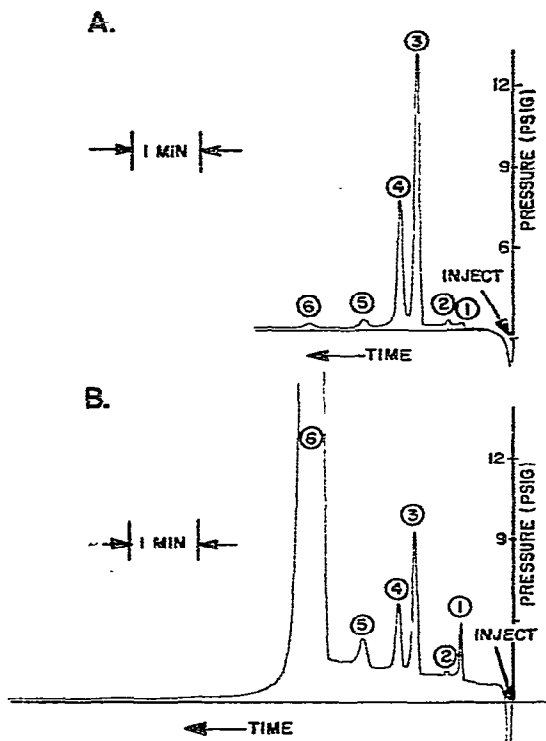
A.

B.

Fig. 1. Chromatographic signals obtained as the difference between reference and sensing orifices. (A) Hydrocarbon sample diluted with helium. (B) Pure hydrocarbon sample containing 90% butane. Column, 6 ft. × 0.085 in. I.D., 20% w/w bis(2-ethoxyethyl)sebacate on 80–100 mesh Chromosorb P; ambient temperature; flow-rate, 50 ml/min. 1 = Methane; 2 = ethane; 3 = propane; 4 = propylene; 5 = isobutane; 6 = butane.

where

r = radius of the capillary
L = length of the capillary
η = viscosity of the fluid in the capillary
F = volume flow-rate
K = constant.

Since the capillary does not respond directly to density changes it can be used to sense flow variations in a gas stream of constant viscosity. The capillary compensation can be used in parallel with the orifice (bridge network) or in series. We elected to try the latter approach. The final design is shown schematically in Fig. 2.

The flapper nozzle unit, amplifier relay and feedback bellows shown in Fig. 2 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 in 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 initial disturbing force. Gain is achieved through the area relationships and positions of the
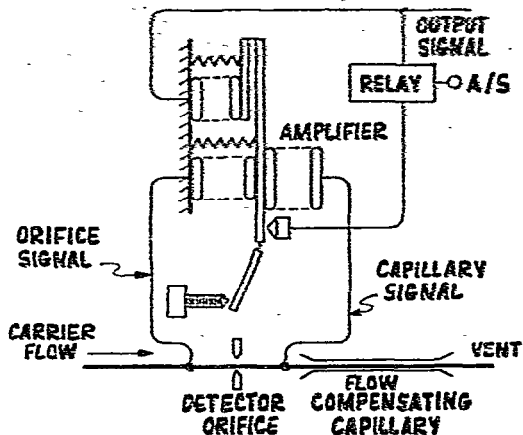
Fig. 2. Orifice-capillary detector and amplifier.

bellows with respect to the pivot point of the lever arm. The output range of the relay is usually 3–15 p.s.i.

In practice it was convenient to obtain compensation at the desired flow by changing the capillary restriction with the appropriate length of 0.008-in. wire. Since the orifice pressure varies as the square of the flow and the capillary pressure varies linearly with flow, compensation could not be precisely achieved at all flows (see
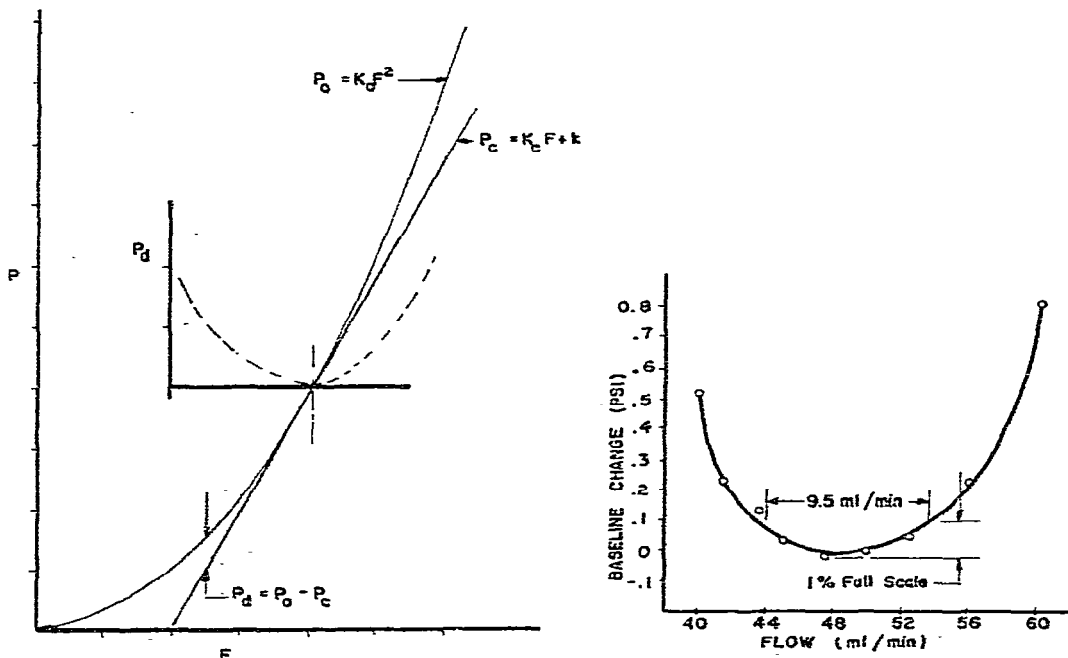

Fig. 3. Flow dependence of orifice and capillary signals, and the origin of the final detector signal. $P_o =$ Orifice pressure; $P_c =$ capillary pressure; $P_d =$ detector signal; $F =$ flow-rate.

Fig. 4. Variation in detector baseline as a function of flow.

Fig. 3). However, as can be seen from Fig. 4, flow changes of 10 ml/min lead at the most to 1 % changes in the baseline position. This was deemed sufficient stability for all but the catastrophic problems. In terms of temperature, a $\pm 5°$ change about a mean temperature of 60° produced a flow change of 1.4 ml/min and a consequent change in baseline of 0.25 % when the system was adjusted to the compensation minimum at 60° and 49 ml/min.

The ability of this detector to compensate for the flow perturbations caused by sample in the column is illustrated in Fig. 5. Note that the large baseline offset which is present in the uncompensated chromatogram shown in Fig. 1 has been eliminated.
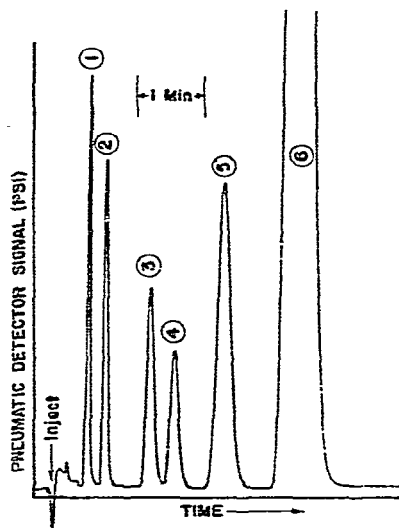

Fig. 5. Orifice-capillary signal for a pure hydrocarbon sample containing 90 % butane.

Detector response —linearity

Since the flow compensator senses gas viscosity in addition to flow, and is an integral part of the detector, the total detector response can be written as

$$\Delta P = A_o K_o F^2 \Delta \varrho - A_c K_c F \Delta \eta + k \tag{7}$$

where

$\Delta P =$ detector signal above baseline
$K_o, K_c =$ lumped orifice and capillary constants
$F =$ volumetric flow-rate
$\Delta \varrho =$ change in density due to sample component
$\Delta \eta =$ change in viscosity due to sample component
$A_o, A_c =$ orifice and capillary gain factors
$k =$ additional force necessary to achieve displacement of capillary flow curve from the origin.

For the analysis of hydrocarbons with helium as carrier gas, $\Delta \eta$ is negative and $\Delta \varrho$ is positive. Thus the signal is the summation of both terms in eqn. 7.
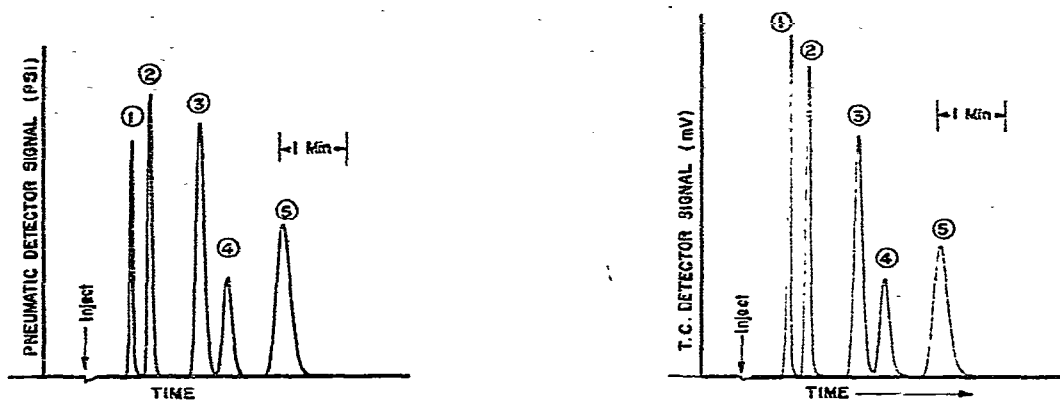
Fig. 6. Orifice-capillary signal for the same hydrocarbon sample shown in Fig. 7.

Fig. 7. Thermal conductivity detector signal for a hydrocarbon sample. 1 = Methane; 2 = ethane; 3 = propane; 4 = propylene; 5 = isobutane.

Chromatograms of identical samples obtained with this detector and a small-volume thermal conductivity (TC) detector are compared in Figs. 6 and 7.

Results for chromatographic analysis of various standard samples are shown in Fig. 8. Linearity was defined as the maximum deviation from a 45° calibration curve secured by setting the gain so that the most concentrated sample in the series registered at 100% of range. For 1-ml samples containing less than 10% of the particular component, detector response was linear to within 1%. The nonlinearities noted at high concentrations were apparently due to a chromatographic problem. The 1-ml sample volume used for all samples resulted in a column overload and distorted peaks at the higher sample concentrations. Similar nonlinearities were obtained when the same column was fitted into an HP-3750 chromatograph equipped with a flame ionisation detector and 1-ml sample loop.
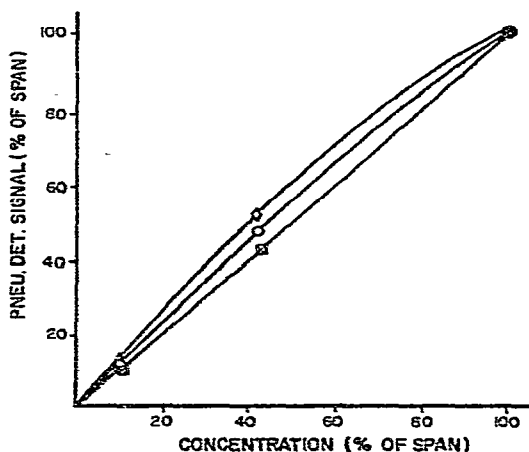

Fig. 8. Linearity studies with the orifice-capillary detector. ×, 0–1% C_3H_8 range; □, 0–10% C_3H_8 range; ○, 0–22% C_3H_8 range; ◊, 0–47% C_3H_8 range.

The gain of the amplifier was changed by varying the pivot position of the lever arm (screwdriver adjustment) and was not amenable to auto-ranging. Thus large dynamic ranges were not automatically attainable. However, for process control, large changes in process stream composition are not usually encountered and thus lack of auto-ranging was not expected to be a disadvantage.

As mentioned previously, it was decided that a minimum change of signal of 0.08 p.s.i. should register as a 12 p.s.i. change in pressure at the output. This requires an amplification of 150 and is a considerable fraction of the open loop gain available to most pneumatic amplifiers. However, since a second peak height amplifier is available in the peak processor portion of the final system, it is not necessary to take all of the 150 gain on one amplifier. Current operating practice uses a gain of 20–30 on the detector amplifier and a gain of 5 on the peak height amplifier.

Temperature sensitivity

It is well known that column flow changes with temperature in a manner that compensates for changes in retention volume due to temperature variation in the partition function. However, this compensation is fairly small. Because of the large flow sensitivity of the pneumatic detector response, there was reason to suspect that the peak heights would be less sensitive to temperature with this detector than with a thermal conductivity device.

From the known relationship between retention volume and temperature it can be shown that[2,7]

$$\frac{dV_r}{V_r} = \frac{-k'}{(1 + k')} \frac{\Delta H}{R T_c} \frac{dT_c}{T_c} \tag{8}$$

where

R = universal gas constant
k' = the capacity factor
V_r = retention volume
ΔH = heat of solution
T_c = column temperature

also for Gaussian peaks

$$dV_r/V_r = -dh/h$$

where h = peak height.

The flow dependence of the response of a detector (D) can be written as

$$D \propto h \propto F^\varphi$$

Then

$$dD/D = dh/h = \varphi \, dF/F$$

Since flow is inversely proportional to viscosity, which in turn varies with temperature, as $T_c^{0.8}$

$$dh/h = -0.8 \, \varphi \, dT_c/T_c$$

Thus the total variation in peak height due to the temperature sensitivity of flow and retention volume is

$$\frac{dh}{h} = \frac{k'}{(1 + k')} \frac{\Delta H}{R T_c} \frac{dT_c}{T_c} - 0.8 \, \varphi \, \frac{dT_c}{T_c} \tag{9}$$

For TC cells φ is usually negative and thus the flow dependence aggravates the problem. For the pneumatic detector φ is approximately 2.

The results of a set of experiments comparing the temperature sensitivity of the pneumatic detector with a TC detector shown in Fig. 9 are consistent with the above prediction.
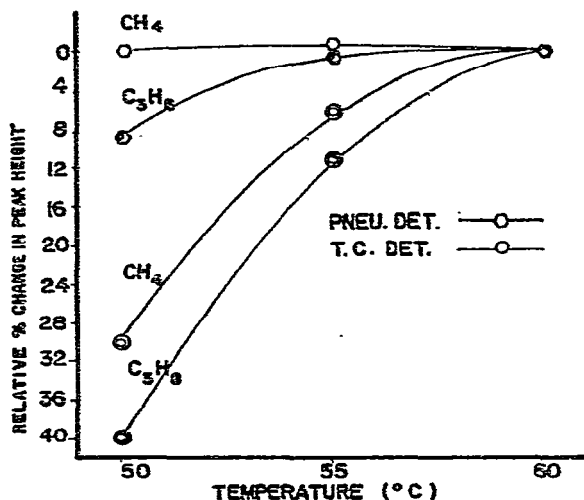

Fig. 9. Comparison of the temperature sensitivity of the orifice-capillary and thermal conductivity detectors.

OVEN AND TEMPERATURE CONTROL

The small temperature coefficient for the detector, coupled with the use of the yet-to-be-described self-adjusting programmer, simplified the oven design since it reduced the temperature specifications on the oven and control system from the $\pm 0.2°$ of electronic models to $\pm 1°$ for the pneumatic system.

A detailed discussion of the oven and controller system will be published elsewhere. It is schematically illustrated in Fig. 10. Energy was supplied from 30 p.s.i. steam through the heat exchanger. Control was achieved with a no-moving-parts pneumatic fan through a controlling element which consisted of a flapper (A) made of temperature-sensitive bimetal and a nozzle (B). The force on the nozzle was generated by the spring constant of the flapper. Below the set-point temperature the nozzle was blocked causing full 20 p.s.i. output at the relay which in turn fed a nozzle situated at the entrance to the heat exchanger.

The high-velocity air molecules emerging from this nozzle momentum interchanged with other low velocity molecules, thus creating a large volume movement of air through the exchanger into the oven. As temperature approached the set point, the flapper began to move away from the nozzle, thereby decreasing the relay output and consequently decreasing the exchanger throughput. At set point this system operated in a proportional mode giving sufficient air movement through the exchanger
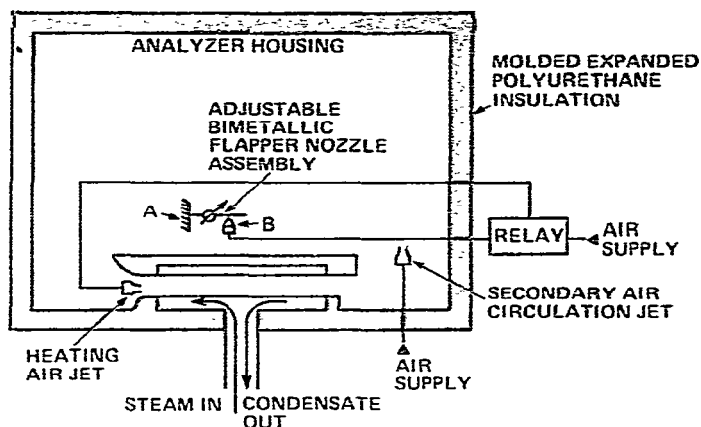
Fig. 10. Pneumatically controlled steam heated enclosure.

to maintain the desired temperature. Oven temperatures were easily varied by changing the spring force on the flapper.

With the oven thermostat set at 75°, average column temperatures were found to be stable to 1.5° over ambient temperature swings of 97° (-32–65°). Chromatographic peak heights under these conditions varied by less than the 1 % measurement error.

SAMPLE VALVE

The sample valve was a pneumatically actuated two-position, ten-port slider type. The slides were manufactured of fired Al_2O_3 and lapped to optical flatness. This material is extremely hard and eliminated the problems of scratching and consequent leakage experienced with PTFE-faced sliders. One valve performed the function of both sample inject and back-flush valves. The two common configurations are shown in Fig. 11. The valve was found to be extremely reliable —the only significant observation after one million cycles being that the two faces had lapped each other to a greater degree of flatness.

AUTOMATION

A process gas chromatograph must be operated automatically. In this mode it must make a sample injection, switch the valve to the back-flush position at the appropriate time, select the correct peak or peaks, and measure the peak height, update the trend signal with the new information and then repeat the cycle with a new sample. These objectives are summarized in the system diagram shown in Fig. 12.

In order to implement these ideas it was necessary to develop a pneumatic clock, a programmer, and a peak processor. It is not the purpose of this section to discuss in detail the mechanics of the system elements. They were constructed using standard pneumatic hardware although obviously a comparable electronic system is possible. Rather it is the manner in which they were used to yield a more reliable and trouble-free system that is of interest here.
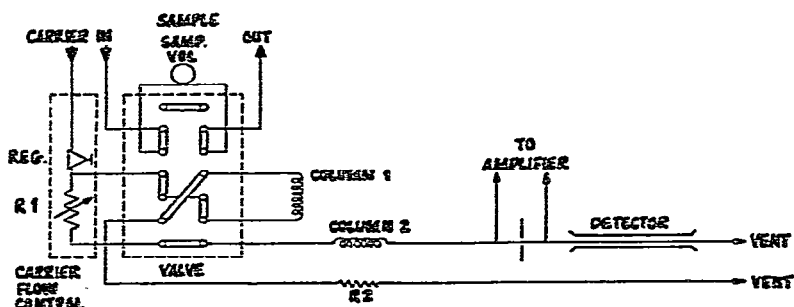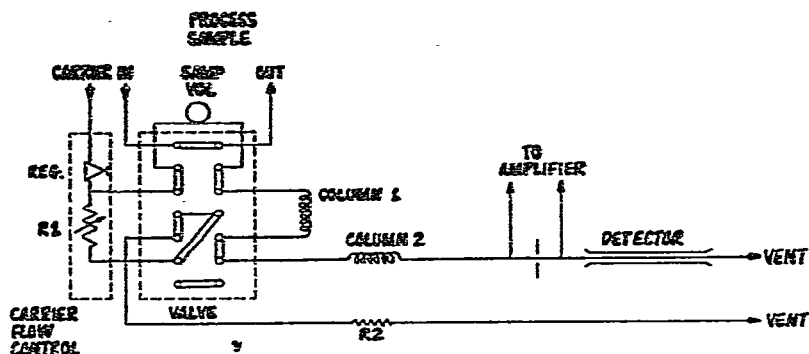
Fig. 11. Schematic representation of the sample fill and sample inject positions of the sample valve.

PNEUMATIC CLOCK

A linear time-dependent pressure signal was obtained with a simple constant input flow integrator. Since the gas flow and consequent ramp rate are quite temperature-sensitive, it appeared that the clock would also have to be thermostated. However, as will be shown in the succeeding discussion, this became unnecessary with the programming procedure which was developed during this research.

PROGRAMMER

Except in the case described by one previous report from this laboratory[8], process gas chromatograph programmers are usually designed around an absolute time base. An accurate clock is used to time a sequence of events such as column switching, auto-zero, peak selection, etc.

The problem with this approach is that peak retention times are not constant. They vary with changes in column load (aging), flow, or temperature. Since it would be disastrous to start controlling the process on the wrong information, this necessitates periodic manual reprogramming of the unit.

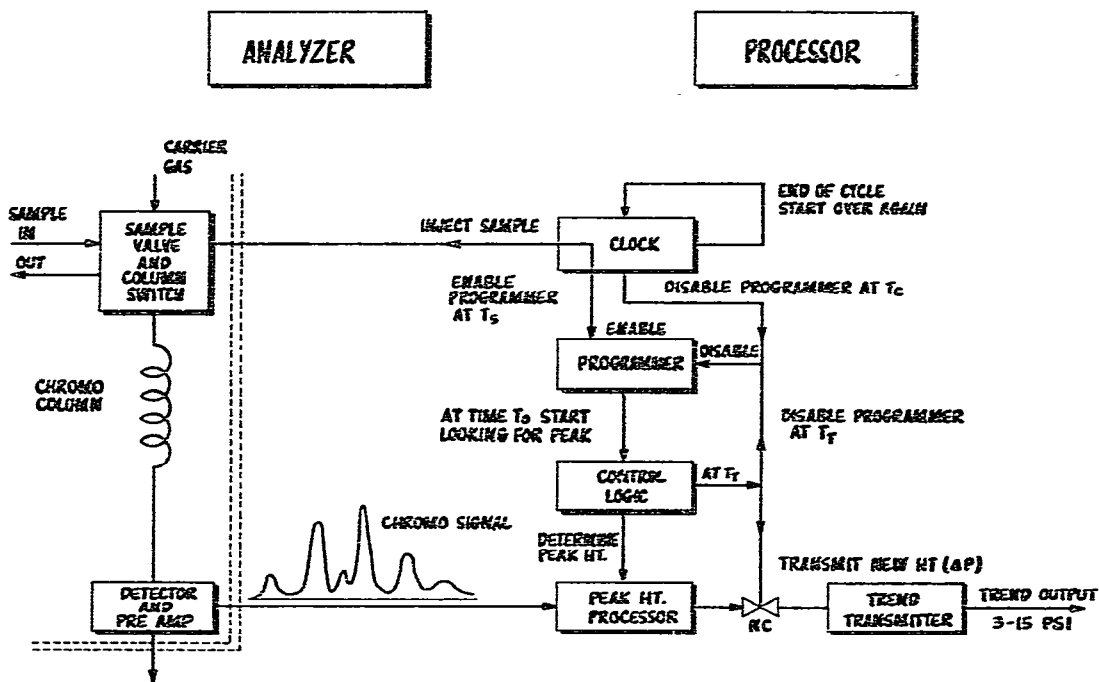Some attempt has been made to provide continuous adjustment of the program

Fig. 12. Schematic representation of the system operation.

by automatically changing temperature or flow in order to maintain the peak position at the same absolute time[9].

We have adopted a somewhat different philosophy and that is to automatically change the programmer event time in response to peak movement. This allows faster adaption to changing conditions and is somewhat simpler to implement.

In one embodiment of this approach the peak window is opened at a time based on the appearance of a reference peak[8]. Since relative retention times are fairly constant over large ranges of temperature, flow and column load, this assures reliable peak selection under a variety of conditions.

The present work utilizes the peak of interest as its own reference point and that of the second component. The time (clock pressure) at which this peak appears is memorized and used to create a reference pressure (time) for opening the window to analyze the same peak in the next cycle. Thus, the reference time is one cycle out of date. It is certainly sufficiently current to insure accurate programming except under the most catastrophic conditions.

The relationship of events to the appearance of the chromatographic peak is summarized in Fig. 13. Sample is injected at the beginning of the analysis cycle. Not shown in the diagram is the return of the sample to its "sample fill back flush" position at some selected time in the program. At time T_0, which is usually 90% of the retention time, T_t, of the desired sample component, the control logic activates the differential peak height analyzer. T_0 is adjusted to be anywhere between the top of the preceding peak and the beginning of the selected peak. The differential peak height analyzer tracks the signal and finds the difference between the lowest point and the next high
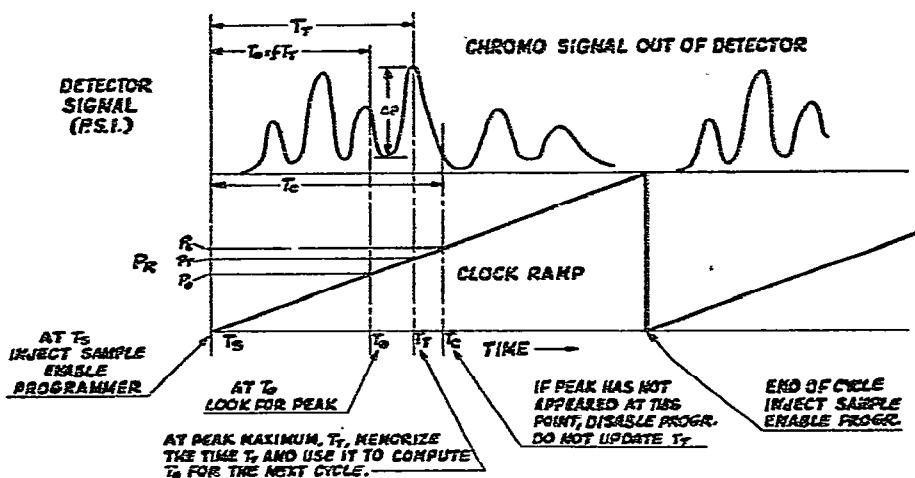
Fig. 13. Relationship of events to the appearance of chromatographic peaks.

point. This differential peak height is then memorized and transmitted as an updated trend signal. In addition, the retention time of the peak is memorized and used to calculate a new T_0 for the next cycle. Thus the peak window is constantly being automatically adjusted for small movements in peak position due to changes in temperature, flow, column load, etc. The auto-zero also "floats" since it is the lowest point after the differential peak height analyzer is enabled. The program is protected by disabling the programmer if a detectable peak has not appeared by time T_c. It is also protected against air failure by using a mechanical memory to store T_r.

Large, abrupt changes in retention time cannot be accommodated if the shift is so large as to have T_0 appear earlier than the previous peak maximum or on the leading edge of the selected peak. The only system variable that could possibly change fast enough to accomplish this would be flow.

The advantage to the above approach is that the system not only adjusts itself for chromatographic retention time shifts but also for shifts in performance of the mechanical components of the system due to varying temperature, changing restrictor resistances, etc. In terms of design, it meant that the pneumatic clock, programmer and processor units did not need to be thermostated. The ambient temperature tests (-32–$65°$) referred to under the section on oven design were conducted on a completed system containing the clock programmer, and peak processor in a separate non-thermostated package. Although clock ramps varied by more than 10% over this temperature range, programming accuracy was not affected.

FINAL DESIGN AND PERFORMANCE

As the result of the research described herein, a commercial pneumatic process stream composition transmitter has become available. A recent report discusses the mechanics in a little more detail than presented here, and the results of field trial evaluation of six production units are also given[10].

CONCLUSIONS

In summary, a new look at implementing design criteria for process chromatographs has resulted in the synthesis of a new and unique system which should have a significant impact in the field of process control.

The development of a rugged and accurate pneumatic detector, the use of standard pneumatic control technology and the introduction of a novel chromatographic programming philosophy lead to a compact design of improved reliability while at the same time offering the advantages of easy maintainability, safety, immunity to electrical interference, and economy.

REFERENCES

1 R. Villabos, *Anal. Chem.*, 47 (1975) 983A.
2 M. Goedert and G. Guiochon, *J. Chromatogr. Sci.*, 7 (1969) 323.
3 J. H. Griffiths, D. James and C. S. G. Phillips, *Analyst (London)*, 77 (1952) 901.
4 J. Novák and J. Janák, *U.S. Pat.*, 3,354,696 (Nov. 28, 1976).
5 P. C. Haarhoff and H. J. van der Linde, *Anal. Chem.*, 37 (1965) 1742.
6 N. Dyson and A. B. Littlewood, *Anal. Chem.*, 39 (1967) 638.
7 M. Goedert and G. Guiochon, *Anal. Chem.*, 42 (1970) 962.
8 R. Annino, *J. Chromatogr. Sci.*, 8 (1970) 288.
9 F. D. Martin, *Instrum. Tech.*, June No. (1972) 46.
10 A. W. Waters, R. Annino, R. C. Prescott and E. L. Karas, *Proc. IMEKO Congr., 7th, London, May 1976*.