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Industrial-grade field-mountable gas chromatograph for process monitoring and control

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Abstract

A novel design is proposed for a field-mountable on-line process gas chromatograph. The chromatograph proper is constructed as a light, portable, plug-in cartridge in support of a rapid repair-by-replacement philosophy. The support structure is mounted close to the sampling point and consists of an explosion-proof section and an intrinsically safe oven that can be unbuttoned in the field without powering down the unit. The “cartridge” chromatograph is designed to support fast capillary column chromatography. A description of a prototype unit is given as well as performance chromatograms and a demonstration of its multicolumn analysis capability by its application to the rapid BTU (British Thermal Unit) analysis of natural gases.

1. Introduction

The differences that distinguish on-line process gas chromatography (PGC) systems from their laboratory counterparts have been discussed in the literature [1–3] and details for the design and operation of industrial-grade PGC systems can be found in a recently published text [4]. These analyzers are designed with the objective of providing up-to-date composition measurement information to enable proper control of the process.

The purpose of this paper is to propose a design for PGC systems that will better meet the monitoring and control objectives than have previous devices and to report our progress toward attaining this goal. This report will focus specifically on the design and performance of the analyzer (chromatograph) portion of the package.

The primary research goal was to design and test a truly field-mountable (FM) PGC systems that had the following attributes. It would (1) require none of the usual on-site trouble-shooting and repair that is common with currently manufactured PGC systems, (2) be truly field mountable (on a pipe stand) close to the sampling point, (3) provide updated analysis to the control system in seconds rather than minutes.

It was assumed early on in the research that there was no way to design a unit that would be maintenance free. It was anticipated that both user misuse, as well as unexpected process upsets, would continue to pose problems for the FMPGC system well into the future. Thus, to limit the exposure of maintenance personnel to the elements, a design was required that would allow for rapid replacement of the unit in the field rather than trouble shooting and replacing individual components as is the practice today.

It was decided to design the analyzer so that there was only one rapidly replacement part. This part would include as a unit the columns, detector and sample/switching valves. The support structure consisting of the temperature controlled oven, calculation/communication/control section, and the basic sample-handling support structure would remain intact at the site.

Short analysis turnaround times would be insured by both short sample transport lines and an analyzer design that would support chromatography on 0.25 mm to 0.050 mm I.D. open tubular columns (OTCs).

2. Experimental

2.1. General description of the FMPGC system

The proposed FMPGC system illustrated in Fig. 1 is shown with its insulated oven cover unbuttoned and partially removed. The exploded view shown in Fig. 2 illustrates the separation of

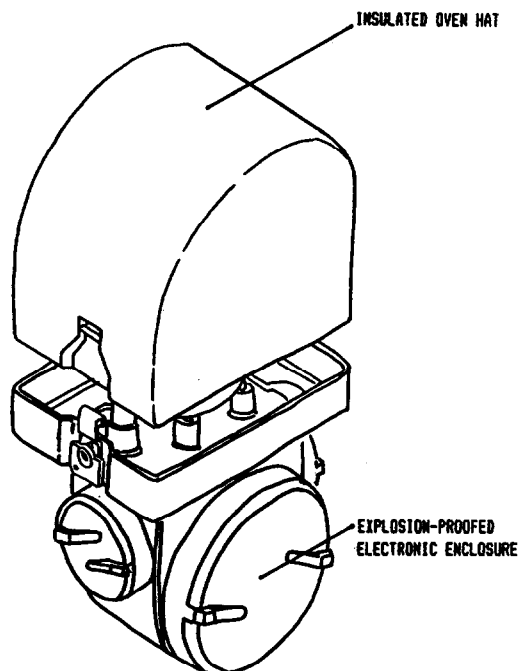


Fig. 1. Complete FMPGC package with GC oven's protective. Covering partially removed.

the intrinsically safe oven enclosure from the explosion-proofed electronics/communication module.

The oven, contained in the upper portion of the field-mounted support structure, is designed for static heating (thus eliminating yet another operating expense and customer burden, i.e., purge air). The oven housing includes a number of electrical heaters cast within its walls for maintaining the temperature of the environment surrounding the chromatograph. The power connections to these heaters as well as to the detector, sample/stream switching valves solenoid drivers, and associated electronics are made below, within the explosion-proof section. Thus, since not enough power is available within its environment to cause an explosion, the oven enclosure is intrinsically safe and can be unbuttoned in the field without powering down. This feature enables the maintenance technician to quickly replace a faulty GC cartridge and have the FMPGC system operational again in a very short time—a critical requirement for control applications.

The analyzer portion of the unit consisting of valves, columns, flow balancing restrictors and thermal conductivity detectors is configured on a manifold so as to form a modular unit that can be replaced easily. This cartridge assembly (shown in Fig. 2 in an exploded view) is lightweight and portable. It is attached in the oven enclosure to two posts (passages through these posts supply carrier gas, sample and vents for the analyzer) by means of two bolts. Thus, it can be easily removed, replaced with another unit and repaired later at a remote site. The individual components of the analyzer cartridge are surface mounted and can be easily replaced in the user's own maintenance shop or returned to the manufacturer for repair.

The idea of using a cartridge totally micromachined of silicon [5], while attractive at first glance, was ruled out for a number of reasons. Very few, if any users, have this technology available in house. Thus, either a manifold unit (consisting of valves, detectors and restrictors, but detachable columns) would have to be made cheap enough to be a "throwaway" item

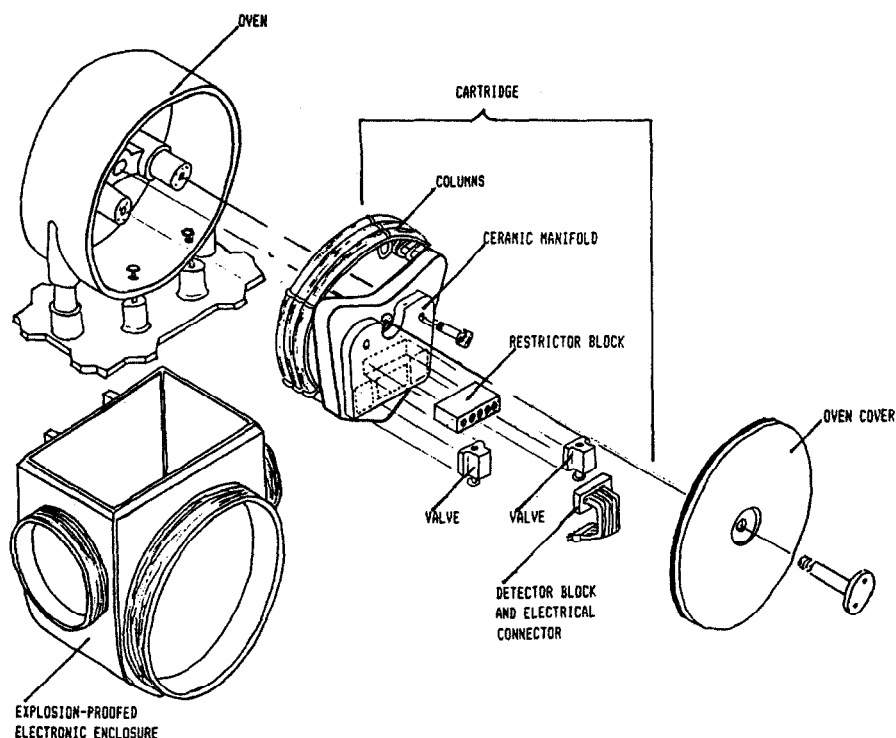


Fig. 2. Detailed view of the FMPGC system showing (as an exploded view) the elements of the cartridge and how it fits into the oven enclosure.

(not likely in the near future) or it would have to be sent back to the manufacturer for repair at additional expense. In addition, in order to accommodate a short turnaround repair time, a large inventory of spare cartridges would have to be kept on hand. We did not, however, rule out micromachining for specific parts of the unit.

2.2. Details of the GC cartridge

No-wrench replaceable chromatograph cartridge

Clearly, the cartridge concept, with its fixed geometry, will not provide the analyst with the flexibility in column, valve and detector arrangements that is now available in current PGC designs. The circuit shown in Fig. 3 was selected as the best compromise to this situation. It features two ten-port valves to be used for sample injection and column switching, balancing adjustable restrictors, and a bank of five thermal conductivity detectors. This circuit pro-

vides the unit with a powerful analysis capability as will be illustrated further on by its application to the measure of the calorific value of natural gas.

The cartridge consists of a chassis plate to which a manifold is coupled. The cartridge is fastened to the oven housing through the chassis by two bolts that are threaded into the bosses in the oven housing. The bosses also contain passageways for carrier gas, sample and vents. The gasketed faces of these bosses mate directly to the manifold to provide a simple leak-free connection of the services to the manifold.

The manifold is made of ceramic by means of the same technology perfected for manufacturing fluidic logic devices (Fluidics Products Department, Corning Glass Works, Corning, NY, USA) and is polished to a flat finish (two light bands interference pattern) to accept the sliding faces of the sample/column switch valves.

It is essentially a pneumatic circuit board and

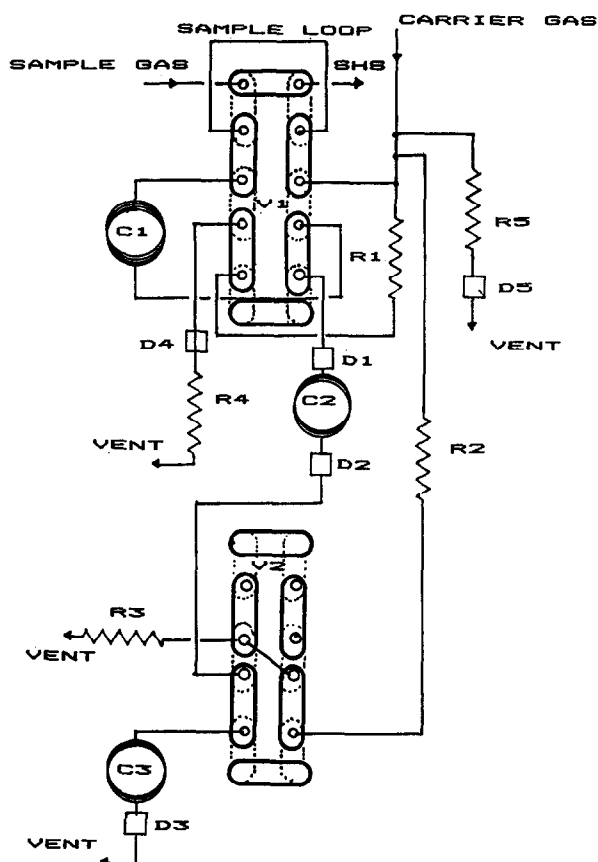


Fig. 3. Flow schematic of the circuit used in the FMPGC system. In the present position of valve 1 (V1) and valve 2 (V2), a portion of the process stream from the sample handling system (SHS) is being sent back to the SHS where it will be either returned to the process or vented. The injected sample of the process is being directed to columns C1, C2 and C3 and detectors D1, D2 and D3. The flow schematic for V1 in the backflush position and V2 in the stream divert position is given by the dotted lines (C1 is backflushed to vent through D4 and R4 and the remaining components in C2 are diverted to vent through R3 while the remaining components in C3 are eluted and detected by D3).

contains the connecting channels (0.015 in. I.D.; 1 in. = 2.54 cm) and holes (0.010 and 0.015 in. I.D.) for the columns, detectors, restrictors and valves that are surface mounted on it (see exploded view of the cartridge in Fig. 2).

Cartridge elements

Columns

Provision is made to support multicolumn

analysis schemes using conventional fused-silica open tubular (FSOT) and micropacked columns. In order to retain user flexibility of column selection and replacement, the columns are not directly connected to the manifold. Rather the connection is made via standard 1/16-in. Valco capillary column connectors to stainless-steel column blocks that are themselves surface mounted on the manifold.

Injection and column switching valves

Even though fairly detailed operating characteristics of the no-moving part fluidic sample valve suggested by Gaspar et al. [6] are available [7], the use of this technology was ruled out because it requires the sample to be at an elevated pressure (the sample pressure in the fluidic valve must be larger than the column head pressure). Thus, to encompass applications where the sample is at atmospheric or lower pressures provision would have to be made to pressurize the sample. Besides the additional hardware required to do this, the pressurization might unduly complicate sampling streams with high dew points.

Based on the results of our previous experience with miniaturized versions of conventional valves and the preferred geometry of the valve in the cartridge, a slider type valve was chosen.

Two slider valves are mounted on the manifold. They are identical and miniature in size. Their Rulon II sliders are finished to 0.3 microns and have 0.020-in. wide slots to transfer gas from the 0.010-in. holes in the manifold to the appropriate channels. The sliders are attached to shafts that mate (through simple fastener free couplings) with those of the solenoid shafts. Switching times for this design were calculated to be less than 5 ms.

Before finalizing the design a prototype of the valve was tested and found to remain within specifications even after one million cycles.

Flow-adjusting restrictors

When using multicolumn analysis schemes, a means of balancing carrier gas flow-rates is

Table 1
Variation of sensitivity with excitation current

Current (mA)	Resistance (Ω)	Sensitivity (mV/mol% propane)	Temperature of filament ($^{\circ}\text{C}$) ^a
7.64	147	22.2	119
9.99	162	30.3	161
12.0	178	38.0	206
13.6	196	43.8	257
15.1	215	51.0	311
16.5	237	57.6	372
16.9	242	59.5	388
17.8	262	63.9	444

^a Temperature coefficient of the sensor was $0.354 \Omega/^{\circ}\text{C}$.

required when switching from one column configuration to another. Five adjustable restrictors are provided for this purpose. They are contained in a stainless-steel restrictor block that is mounted on the manifold. These restrictors are identical and consist of stainless-steel mandrels which ride in plastic sleeves (with a 0.0005-in. interference fit). They are threaded with a variable-depth thread from 0.0035-in. deep at maximum to zero in five and one half turns.

Thermal conductivity detectors

Only four detectors are required to support the configuration outlined in Fig. 3 (a fifth is provided to be used as a reference detector if desired). They are identical, each consisting of a 1- μm platinum wire welded to two posts of a glass-to-metal-sealed header soldered to a brass metal holder. A cavity (approximately 0.08 μl volume) is previously ground (or etched) into the glass under the platinum wire. This open-faced detector block is attached to the manifold and connections to the appropriate holes in the manifold are made through the mounting gaskets.

The nominal room temperature resistance of the detector filament is 100 Ω . The characteristics of a typical detector element are given in Tables 1 and 2.

The slight variation of sensitivity with carrier gas flow-rate that was observed was attributed to the design requirement for a fast responding detector to support high-speed chromatography.

This necessitated placement of the filament in the flow stream with a consequent increase in the specific heat, flow-sensitive, component of the detector signal. In any case, it was felt that the observed flow dependence was not large enough to constitute a problem.

As has been reported elsewhere [8], the rather large time constant of currently manufactured gas chromatographs seriously limits the performance of these systems to support high-speed analysis. Using a large 84- μl sample loop (to create a frontal chromatogram) to inject propane-helium (4.8:95.2) mixtures into the present detector, the time constants (time to reach 67% of the final peak height) at various flow-rates were determined and plotted versus the reciprocal of flow-rate (see ASTM E 516-74 [11]). The intercept of this plot yielded a system time constant of less than 0.5 ms.

Table 2
Variation of sensitivity with flow-rate of carrier gas

Flow-rate (ml/min) ^a	Sensitivity (mV/mol% propane)
1.7	43.9
2.5	44.0
3.2	43.9
4.3	44.4
5.6	44.3
7.0	44.8
8.0	44.9

^a Flow-rate of propane-helium (1:99).

Table 3

Comparison of experimental vs. theoretical peak widths for a system time constant of 5 ms

Component	Flow-rate 3.6 ml/min				Flow-rate 6.9 ml/min			
	Retention time (s)		Peak width (s)		Retention time (s)		Peak width (s)	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Unretained	8.19	8.40	0.14	0.15	4.71	4.74	0.07	0.08
Ethane	8.79	8.80	0.22	0.16	5.06	4.92	0.14	0.10
Propane	9.81	9.60	0.31	0.22	5.65	5.40	0.22	0.16

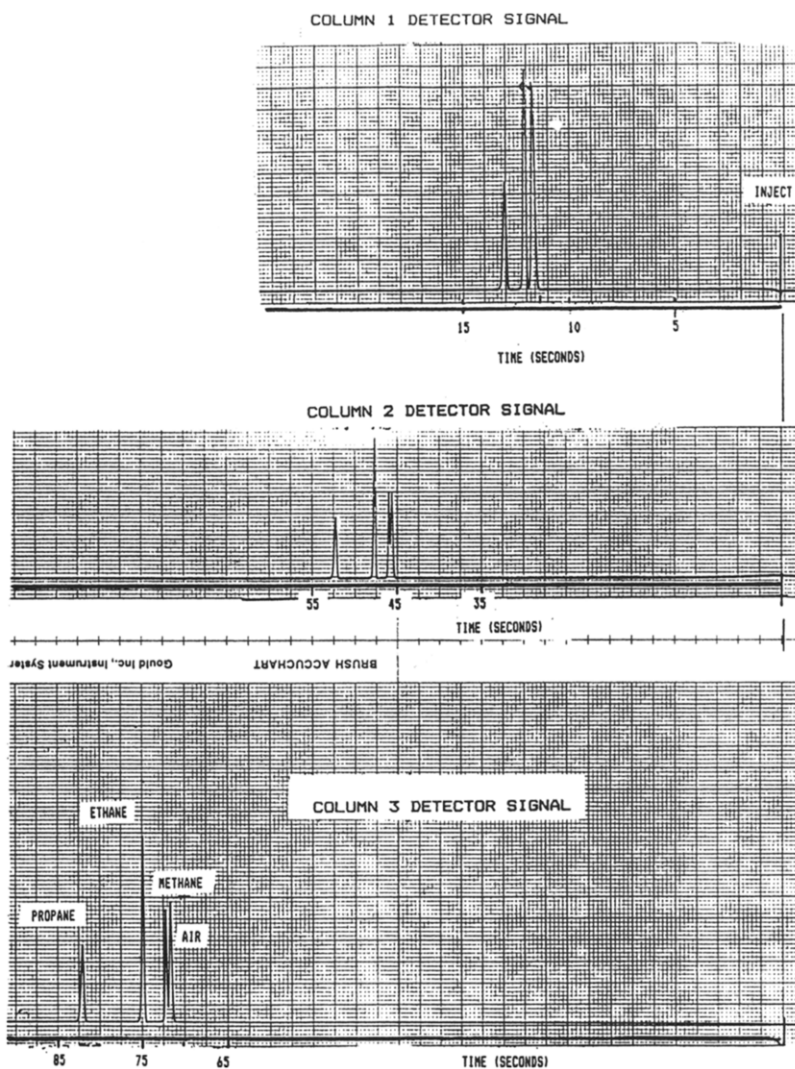


Fig. 4. Performance chromatograms obtained at D1, D2 and D3 for the flow configuration illustrated in Fig. 3. Stationary phase = GB-1 at film thickness $1.0 \mu\text{m}$. FSOT column of 0.25 mm I.D., $C_1 = 7 \text{ m}$, $C_2 = 25 \text{ m}$, $C_3 = 27 \text{ m}$; temperature, ambient; carrier gas, helium at 34.65 p.s.i.g. ($1 \text{ p.s.i.} = 6894.76 \text{ Pa}$); sample: methane-ethane-propane-helium (10:10:8.5:71.5).

To determine the overall system time constant for the normally used impulse injection mode of operation, a sample loop of $0.06 \mu\text{l}$ was used to inject a ethane–propane–helium (10:8:82) mixture into a $7 \text{ m} \times 0.25 \text{ mm}$ I.D., film thickness $1.0 \mu\text{m}$, OV-1 column at various flow-rates of carrier gas. The observed peak widths were compared to that predicted from a theoretical model [9] for systems of various time constants. The closest correspondence was found to be for a system with a 5 ms time constant (see Table 3). This was well within the response that was required to support the projected chromatographic peak widths (50 to 100 ms) for which this unit was being designed.

As mentioned previously, the detectors were powered in the constant-resistance mode. This procedure insured not only a fast responding system, but one that was protected from burnout under large sample loads or when carrier gas was turned off. The time constant for the electronic portion of the package (with the detector element in the circuit) was found to be less than 0.2 ms.

With this system, when the filament was excited to yield a sensitivity of $3.3 \mu\text{V}/\text{ppm}$ (v/v) propane, the peak to peak noise level was found to be $14.9 \mu\text{V}$. Thus, under these conditions the minimum detection level was calculated to be 9 ppm (v/v) propane.

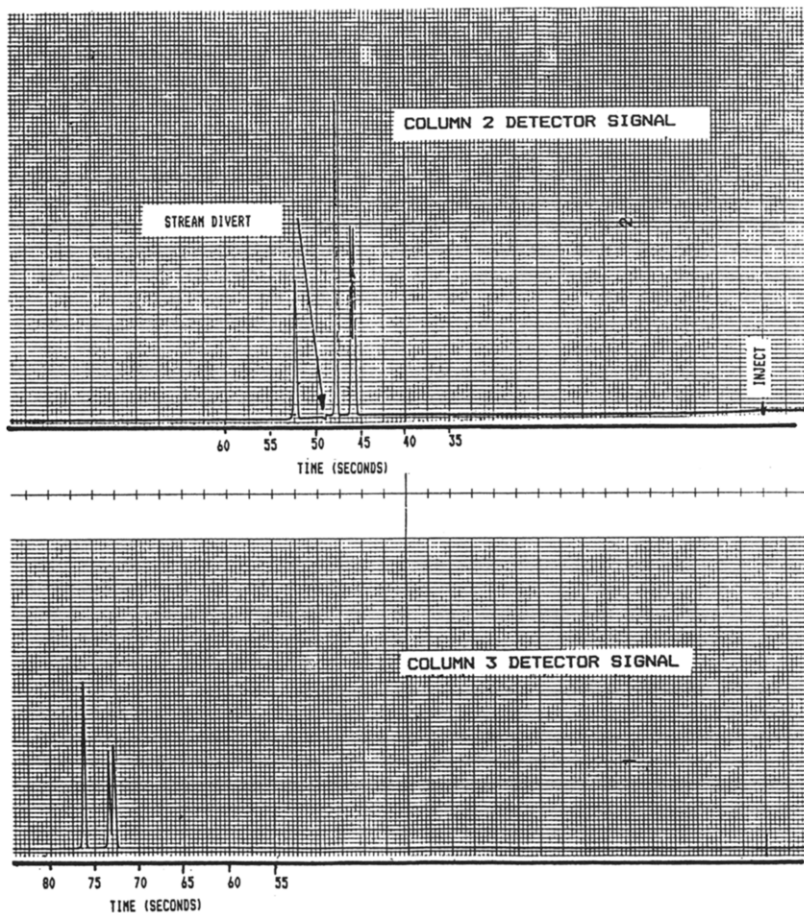


Fig. 5. Performance chromatograms obtained at D1, D2 and D3 when V2 is switched to the divert-to-vent position after the appearance of ethane. Propane is diverted to vent and never enters C3. Thus the chromatogram from D3 contains only air, methane and ethane peaks. Conditions are the same as described for Fig. 4.

3. Results

3.1. Performance of the system

Typical chromatograms obtained from the unit under a variety of column/detector switching arrangements are shown in Figs. 4–6. As can be seen by examining those signal channels that involve column switching, flow balancing was sufficiently accurate to eliminate significant baseline upsets during the switching.

Since many of the flow passages involve rather abrupt 90° changes in direction with consequent changes in the flow profile, it was expected that some degree of peak tailing would result.

And indeed, some asymmetry was observed. For example, a high-speed chromatogram of methane, ethane and propane on a 7.0 m × 0.25 mm OV-1 column of 1.0 μm film thickness produced asymmetries of 1.16, 1.19 and 1.30 for the respective peaks. As will be demonstrated in

the following BTU application, this degree of asymmetry does not seriously limit the performance of the unit.

3.2. Application to the BTU determination of natural gas

The following experiments were performed on a prototype unit similar to that shown in Figs. 1 and 2. However, the electronics enclosure was empty except for the oven-temperature controller, valve solenoids and driver electronics. The detector power supply and data acquisition hardware were breadboarded and external to the unit.

Four columns were used for the British Thermal Unit (BTU; 1 BTU = 1054.35 J) determination of natural gas with the proper I.D., lengths and film thicknesses being determined by our computer-aided multicolumn design program [10]. Three of the columns were analysis columns

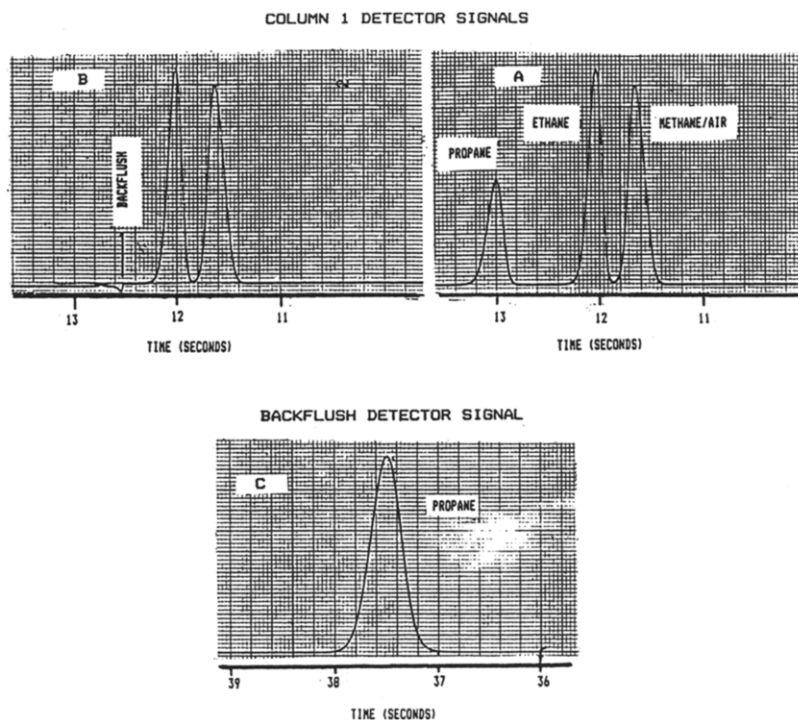


Fig. 6. Performance chromatograms obtained from D1 and D4 illustrate what is observed when V1 is returned to the backflush position after the detection of ethane at D1. Propane is backflushed from C1 and appears at D4. Conditions are the same as Figs. 4 and 5 except that for illustrative purposes a faster chart speed was used to record the chromatograms.

while the fourth, acted only to delay the appearance of any peaks at D3 until after the effluent from D2 had been diverted to vent. This simplified writing the "peak find/analysis" code

since no provision was then necessary to allow for possible baseline perturbations during the stream-switching operation.

The chromatograms simultaneously recorded

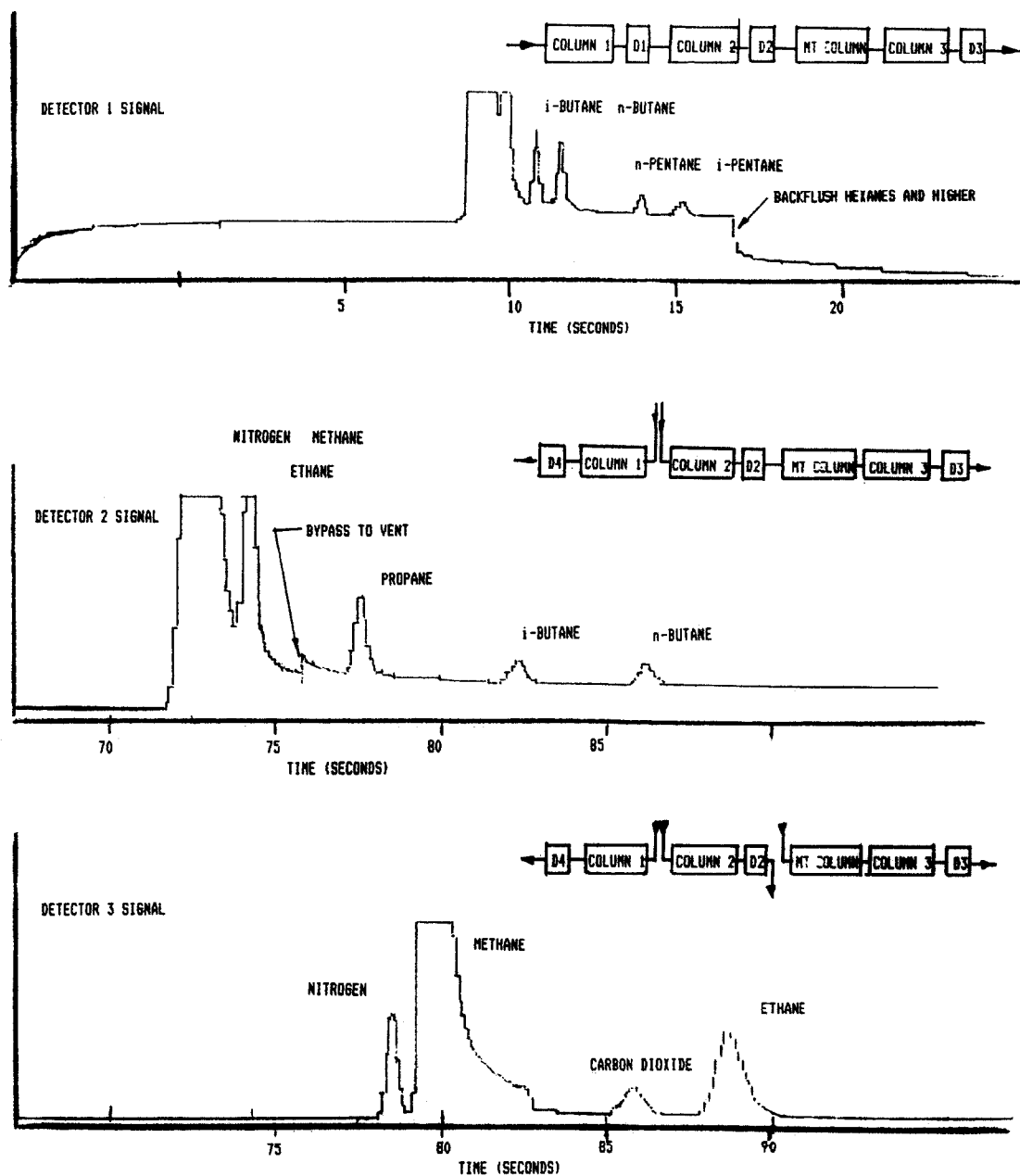


Fig. 7. Chromatograms available at D1, D2 and D3 during a natural gas BTU analysis. GB-1 at $1.0 \mu\text{m}$ film thickness are used in columns 1 ($5 \text{ m} \times 0.25 \text{ mm}$) and 2 ($25 \text{ m} \times 0.25 \text{ mm}$). A delay column of $2 \text{ m} \times 0.25 \text{ mm}$ was used between D2 and the third column [$40 \text{ cm} \times 0.56 \text{ mm}$, 140–170 mesh ($105\text{--}88 \mu\text{m}$), Hayes Sep. T]. Helium carrier gas at 48.5 p.s.i.g.; temperature, 60°C ; sample described in Table 4; i = iso.

Table 4
Standard BTU gas sample

Component	Mol%
Nitrogen	2.52
Carbon dioxide	1.003
Methane	90.64
Ethane	3.99
Propane	0.994
Isobutane	0.302
<i>n</i> -Butane	0.298
Isopentane	0.101
<i>n</i> -Pentane	0.103
<i>n</i> -Hexane	0.050

at the various detectors for a typical analysis along with the pertinent column configurations are shown in Fig. 7. Not shown due to space restrictions is the chromatogram recorded at D4 (the regrouped heavies). Also the full recording of D2 would show the elution of *n*-pentane at 112 s and isopentane at 122 s.

The analysis was conducted at 60°C on a standard BTU sample whose composition is given in Table 4. Helium was used as carrier gas at 4.27 ml/min.

Analysis is complete in just over 2 min—much faster than can be obtained with other analyzers currently on the market. Typically, using a 3-min cycle the analysis of a 1036 BTU/ft³ sample had a standard deviation of 0.87 BTUs/ft³.

4. Conclusions

The successful design of a rapidly replaceable GC cartridge so necessary for a viable FMPGC system has been demonstrated by the results

reported herein. Moreover, this design supports the high-speed chromatography needed for the short turnaround analysis time in control applications.

Acknowledgements

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