Journal of Chromatography, 89 (1974) 1–9
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 7074

A CRYOGENIC GAS CHROMATOGRAPH

JOSEPH A. GIANNOVARIO, ROBERT J. GONDEK* and ROBERT L. GROB**
Chemistry Department, Villanova University, Villanova, Pa. 19085 (U.S.A.)
(Received August 20th, 1973)

SUMMARY

A programmable, cryogenic gas chromatograph has been constructed in this laboratory for use in air pollution studies. Construction of the instrument is modular and utilizes many commercially available components and a few "scratch built" parts. The temperature control range is from −100° to +300° with five programming rates available. The instrument is also capable of dual column–dual detector operation.

Separations of laboratory prepared samples are presented to illustrate instrument versatility.

INTRODUCTION

There have been many reports of separations performed at subambient temperatures[1–7]. In 1963, Merritt and Walsh[8] described a simple, programmed, cryogenic gas chromatograph used in the separation of volatile odors from foodstuffs. In 1964, Merritt *et al.*[9] reported on improvements to their instrument, specifically in the program-rate control. Separations of mixtures of C_1 to C_4 olefins and paraffins, by a technique similar to the one used by Merritt and Walsh, have been described by Baumann *et al.*[10]. Isotopes have even been separated by programmed, cryogenic gas chromatography[11].

These achievements have led to the construction of the instrument described, with the intention of using it for air pollution studies. Cryogenic temperatures are achieved using liquified nitrogen and a solenoid valve activated by a temperature controller. The controller itself has been modified to perform both in the isothermal and programmed temperature mode.

EXPERIMENTAL OPERATION

At conditions above ambient, operation of the instrument is essentially the same as any other gas chromatograph. Temperature is controlled and maintained by a Harrell isothermal controller, Model TC-118-DL (Harrell Inc., East Norwalk, Conn., U.S.A.). In subambient operation, the Harrell unit is still the main controlling device. After setting the desired initial temperature, the controller activates a cryogenic solenoid valve (Asco 8262C22LT-2NC) admitting liquid nitrogen to

---

* Chief engineer, process instrumentation; TOTCO, Glendale, Calif. 91201, U.S.A.
** To whom inquiries or reprint requests should be addressed.

the column compartment. The nitrogen is drawn from a demand regulated siphon tank (Welder's Supply, Philadelphia, Pa., U.S.A.). The demand regulator of the nitrogen flow is critical to the instrument's operation. Each time the solenoid valve is activated, the regulator allows liquid nitrogen to be drawn from the tank. When the solenoid closes, the regulator effectively shuts off the tank, prohibiting the liquid from building up extreme pressures within the piping. A safety release valve is employed since some liquid nitrogen can be trapped between the regulator and solenoid. The regulator is set for a pressure below the 22-p.s.i. safety release pressure.

Several types of cooling methods were employed and discarded before settling upon liquid nitrogen. Using liquid nitrogen provides an efficient and economical means of achieving cryogenic temperatures. One 150-l tank provides enough coolant for *ca.* five days of operation at −35°. As the temperature of the compartment begins to lower, the controller begins to cycle the solenoid valve on and off, yielding a time-proportional cooling rate, until set-point temperature is reached. This time-proportioned on–off action continues to maintain a constant temperature.

Sensing of the compartment temperature for the controller utilizes a multi-element, platinum resistor bridge. This circuit becomes one arm of the internal controller bridge. This arrangement tends to average out local deviations in the column compartment and provides an extremely accurate and reliable temperature reference.

As stated before, in both above and subambient operation, the Harrell unit is the main controlling unit. This unit has been altered to allow both isothermal and programmed temperature control. The set-point potentiometer of the Harrell unit has been replaced by a motor-driven potentiometer, Model 1106S (Valley Forge Instrument Co., Valley Forge, Pa., U.S.A.). The programmer is a temperature setting device for use with a suitable controller (*e.g.* Harrell unit) to control and linearly ramp temperature with time. Several fixed rates are available and a program may be changed, started or stopped at any time during operation. The rates available on our unit are 0.5, 1.0, 2.0, 3.0, 5.0 and 10.0°/min.

The basic controlling action of the Harrell unit is a time-proportioning (on–off) output, in both heating and cooling modes, modified by an automatic reset function. This function tends to avoid overshoot due to high gain but still has the effect of bringing temperature back (automatically resetting) to the set-point. Deviations of 0.5° are easily sensed and compensated.

The combination of time-proportioning the power output to the solenoid and the regulated liquid nitrogen tank has resulted in excellent control of temperature in the cryogenic range. The overall control range is −100° to +300°.

In actual use, the column compartment is allowed to equilibrate to the initial temperature and samples are then injected onto the column and retention times are recorded. At any time during operation a program may be started by simply choosing the desired program-rate and switching from isothermal mode to program mode.

CONSTRUCTION

The instrument is composed of three parts; an electronics module, an oven

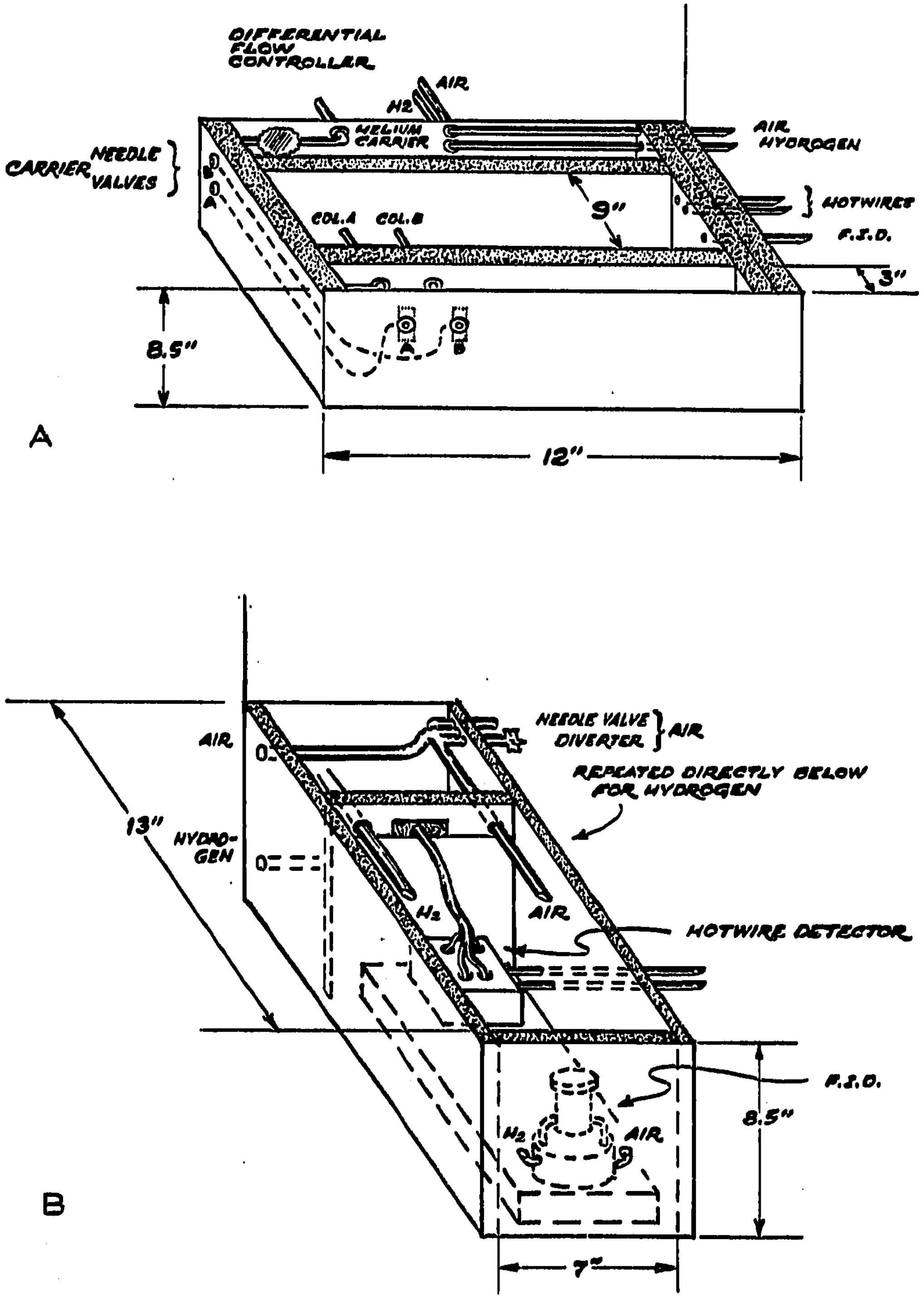

Fig. 1. Oven module. (A) Column compartment; (B) detector compartment.

module and a recorder module. The recorder module is an angle iron framework, housing the recorder and an ionization amplifier, Model 154-0449 (Perkin-Elmer, Norwalk, Conn., U.S.A.). The oven module contains the column compartment (Fig. 1A), detector compartment (Fig. 1B), various flow controls, cryogenic solenoid and fan. Exterior and interior dimensions of the oven module are shown in Figs. 1A and 1B. Both detector and column compartments are insulated with 1.5 in. thick Maronite with a 3-in. wall between the two compartments to insure the stability of the temperature in the detector compartment.

Two heating coils are located in the column compartment behind the fan shroud (Fig. 2). The fan itself is a squirrel cage type to aid in the rapid distribution of heat and coolant, permitting uniform and reproducible temperatures. Coolant is admitted into the compartment and is directed at the fan. The column compartment itself is large enough to accommodate two columns which can be used simultaneously.

Adjacent to the column compartment is the detector compartment, housing both a hot-wire detector (Gow-Mac Madison, N.J., U.S.A.) and a Perkin-Elmer ionization detector, Model 154-0407. Both detectors are in thermal contact with a heated aluminum block for temperature control.

Directly behind the column compartment are the flow controls. The flow controls are comprised of flow controllers, needle valves, flow diverters and associated hardware. The constant flow, differential controllers are essential to an instrument of this nature. Without them, flow-rates would vary erratically over the wide range of program temperatures.

The injection ports were designed by the authors and machined in the chemistry

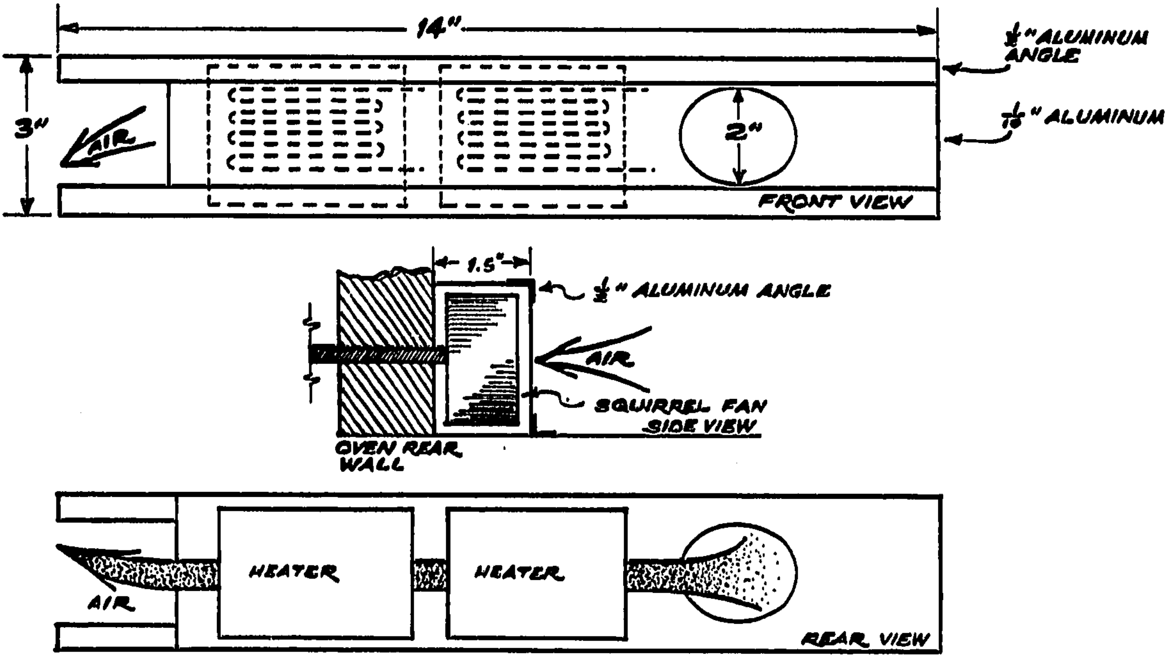

Fig. 2. Fan housing (shroud)

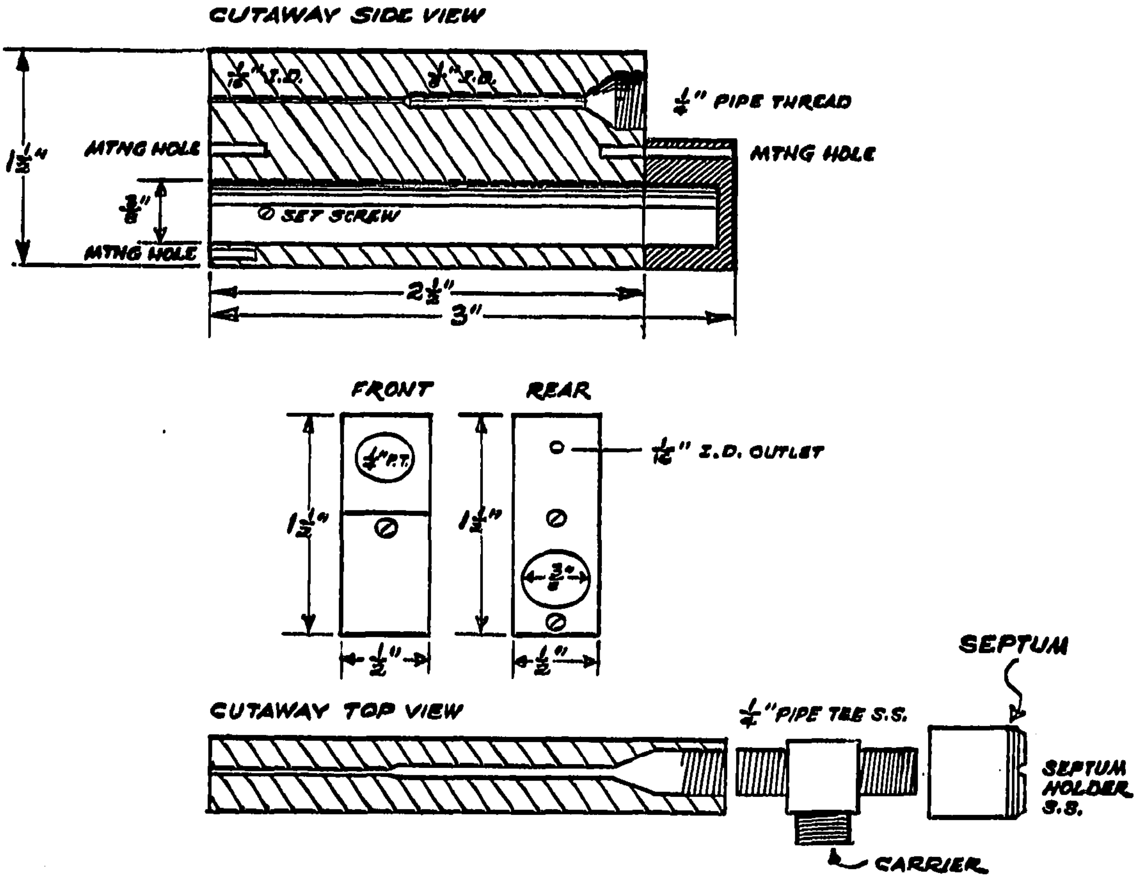

Fig. 3. Stainless-steel injection ports.

department shop. Each port (Fig. 3) is made in two parts for ease of maintenance. The result of this design is efficient heating with good thermal stability.

TABLE I

CONTROLS AND MONITORS FOR INSTRUMENT OPERATION

Controls	*Monitors*
Temperature programmer	Thermocouple selector
Temperature controller	High- and low-temperature pyrometer
Hot-wire power supply	Hot-wire current meter
Hot-wire current adjustment	Column heater pilot lamp
Recorder zero	Column coolant pilot lamp
Signal attenuator	Master power pilot lamp
Heating power to detector block	
Heating power to injection ports	
Master circuit breaker	
Master power switch	

Air and hydrogen, for the flame ionization detector (FID), are directed to the needle valves and flow diverters (Envirotech Corp. L-203-A, Mountain View, Calif., U.S.A.). These diverters act as two-way valves and allow flow-rate measurements without disturbing the FID unit.

Piping for both compartments is shown in Figs. 1A and 1B.

The electronics module contains all the necessary controls and monitors for instrument operation. These are listed in Table I and shown in Fig. 4. The electronics module itself is supported by an angle iron framework which straddles the oven module. Electrical connections employ terminal strips on both modules and multistranded cables terminated in cable plugs.

The instrument can be placed anywhere as long as the liquid nitrogen tank is within reasonable distance. All piping between the tank and the instrument is covered, first with styrofoam, then with glass wool and finally with asbestos tape.

RESULTS AND DISCUSSION

The separations presented were achieved on a 6 ft. × 6 mm O.D. glass column packed with 33% DC-550 on 60–80 mesh Chromosorb W, AW, DMCS. The flow-rate, in all cases, was 33 cm^3/min. The hot-wire detector was employed. Current to the detector was 240 mA and an attenuation of eight was used. Initial temperature was −35°.

Two gas mixtures were prepared to illustrate the instrument operation.

Mixture I contains the inorganic gases CO_2, N_2O, H_2S, COS and SO_2. Fig. 5A is the chromatogram of mixture I run isothermally at −35°. This low temperature was necessary to separate the CO_2 and N_2O peaks; and even at this temperature they are not fully resolved. The effects of this temperature on the other components are increased retention times and severe band spreading; especially in the case of SO_2. Fig. 5B is a chromatogram of the same mixture utilizing a temperature program starting at −35°. After injection of the sample, temperature was maintained isothermally at −35° until the CO_2 and N_2O peaks were eluted.

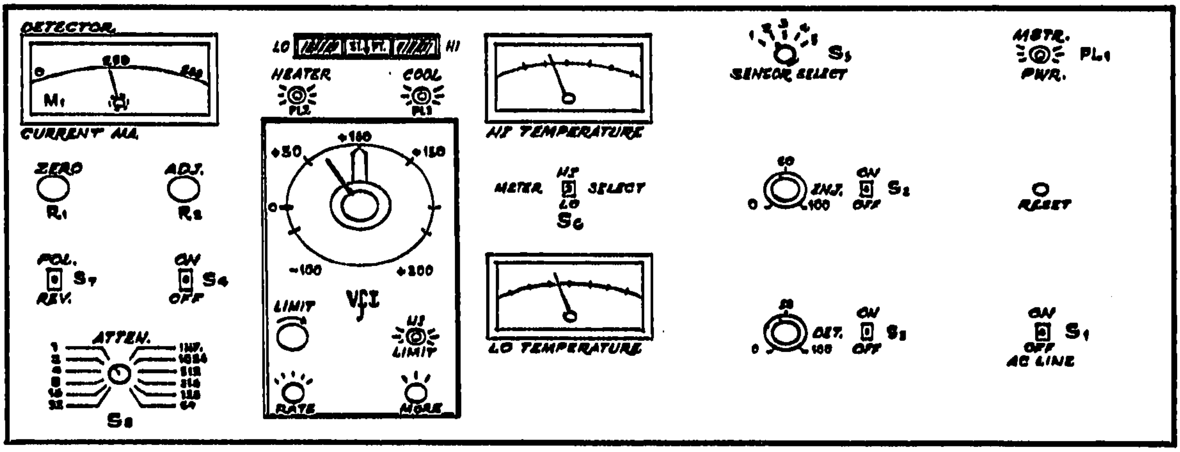

Fig. 4. Electronics module, front panel.

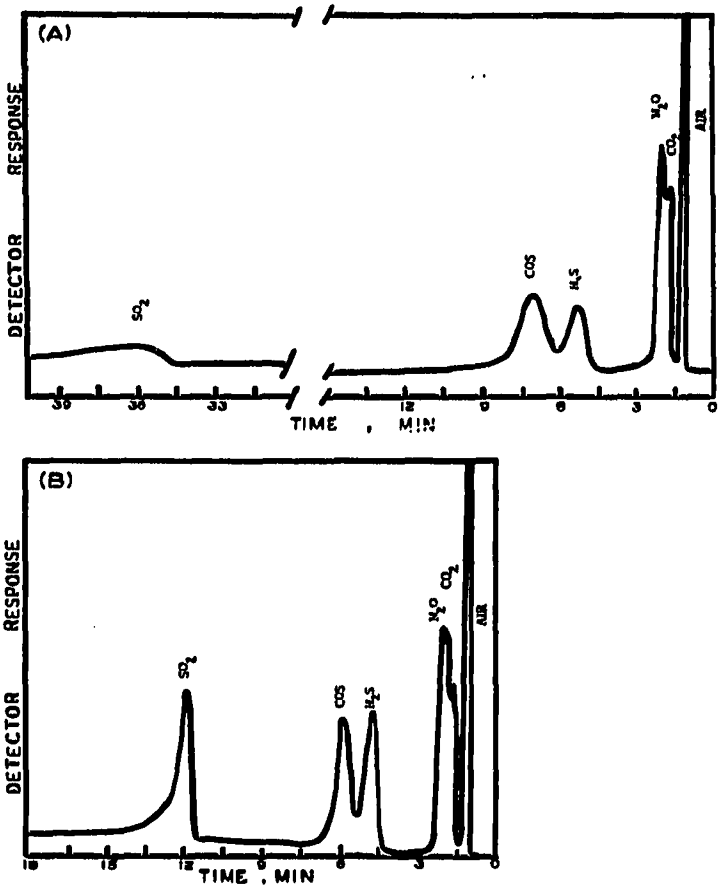

Fig. 5. Separation of some inorganic gases. (A) Isothermal mode, temperature −35°; (B) programmed mode, temperature 3 min at −35°, then programmed at a rate of 5°/min.

Programming was then initiated at a rate of 5°/min until the SO_2 peak was eluted. The result is that all the component peaks are sharpened and exhibit shorter retention times. Most dramatic is the change in the retention time for SO_2, which was roughly halved.

Fig. 6A in the isothermal chromatogram of mixture II, which contained the light hydrocarbons; ethane, propane, isobutane and butane. The isobutane and butane peaks exhibit severe band spreading. Fig. 6B is this same mixture under temperature programmed conditions. Again, all component peaks are sharpened with a corresponding decrease in retention time. Methane is not separated from the air peak under the conditions presented. The utilization of the FID will give us the methane content of the mixture.

CONCLUSIONS

The addition of cryogenic temperature control can increase the operating range of any gas chromatograph. Couple this extended range with temperature program-

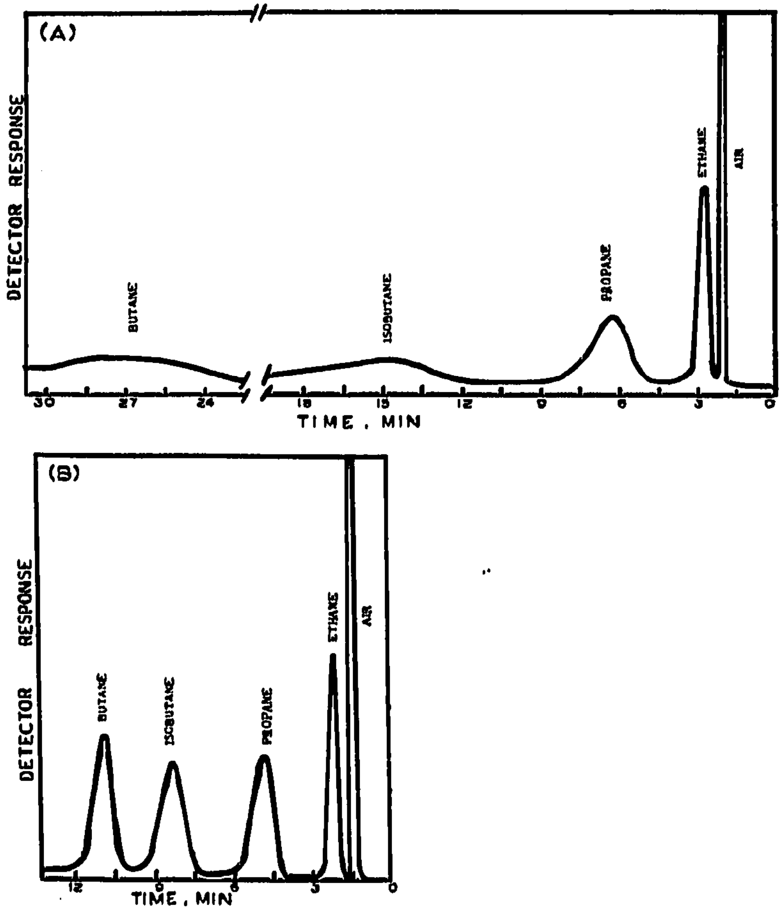

Fig. 6. Separation of some organic gases. (A) Isothermal mode, temperature −35°; (B) programmed mode, temperature −30°, then programmed at 5°/min.

ming and the operator now has another variable that he can manipulate to achieve a desired separation. Additionally, cryogenic operations allow the use of liquid phases that may have proved unsuitable at ambient temperatures and higher.

Cryogenic, programmable gas chromatography can provide researchers with an instrument of long range capabilities. Separations of atmospheric gases to everyday routine analyses could be performed simply by changing columns and temperature.

The separations already achieved on this instrument have led the authors to believe that it can be a powerful tool for use in air pollution studies. Efforts are now being directed toward this goal.

REFERENCES

1 R. S. Porter and J. F. Johnson, *Anal. Chem.*, 33 (1961) 1152.
2 G. Manara and M. Taramasso, *J. Chromatogr.*, 65 (1972) 349.

3 L. E. Heidt and D. H. Ehhalt, *J. Chromatogr.*, 69 (1972) 103.
4 R. A. Herbert and A. J. Holding, *J. Chromatogr. Sci.*, 10 (1972) 174.
5 A. J. Gully, R. R. Graham, J. E. Halligan and P. C. Bentsen, *Report NASA CR-2132*, NSCRAQ (1973).
6 C. N. James, *Anal. Chem.*, 39 (1961) 1858.
7 C. C. Borland and E. D. Schall, *J. Ass. Offic. Agr. Chem.*, 42 (1959) 579.
8 C. Merritt and J. T. Walsh, *Anal. Chem.*, 35 (1963) 110.
9 C. Merritt, J. T. Walsh, P. Issenberg and K. J. McCarthy, *J. Gas Chromatogr.*, 2 (1964) 314.
10 F. Baumann, R. T. Klaver and J. F. Johnson, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 152.
11 A. Purcr, R. L. Kaplan and D. R. Smith, *J. Chromatogr. Sci.*, 7 (1969) 504.