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Apparatus for Programmed Cryogenic Temperature Gas Chromatography

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The development of a technique for separating multicomponent mixtures of highly volatile compounds by programmed temperature gas chromatography in the low temperature range—that is below room temperature—has been described in previous communications (1, 2).

The programming method used in this early work was quite simple. A U-shaped, glass, chromatography column was placed within a cylindrical glass jacket and a suitable coolant, for example, a mixture of solid carbon dioxide and ethanol, was poured into the jacket surrounding the column. The samples were injected on the cold column or swept onto the column from a gas trap with carrier gas. Elution was then allowed to proceed as the temperature gradually increased. There are two obvious limitations to this apparatus. First, the rate of temperature rise is restricted to that obtained by spontaneous warming of the coolant mixture. Second, since there is no provision for heating the column, temperatures cannot be raised above room temperature. There are other disadvantages. Coolant solutions cannot be relied upon to maintain very low isothermal temperatures or to program the temperature in a manner suitable for good retention time reproducibility. Moreover, these solutions often require considerable

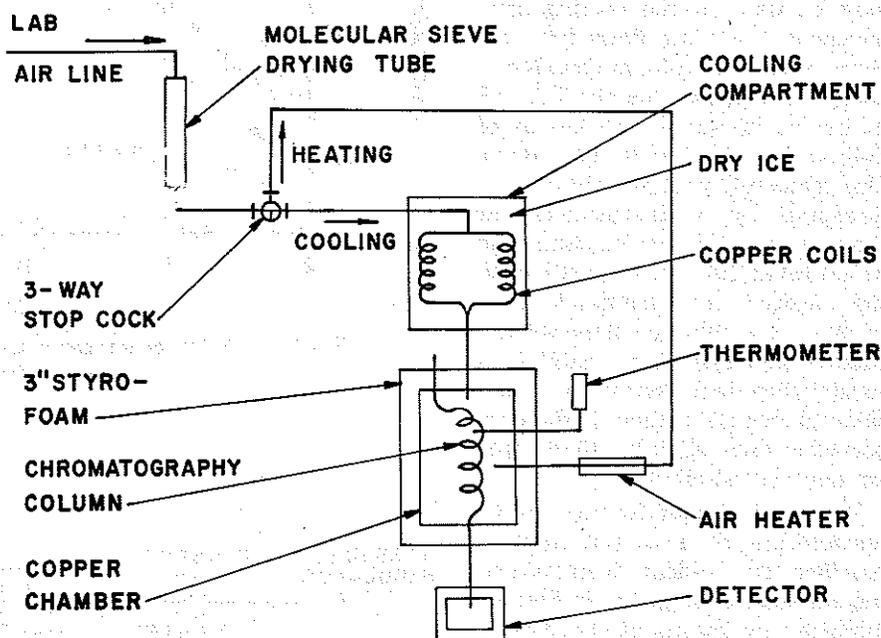


Figure 1. Diagram of programmed cryogenic temperature gas chromatography apparatus employing mixed air streams.

preparation time and are difficult and messy to handle. Since samples analyzed in this laboratory often consist of mixtures of compounds of wide boiling range and a variety of chemical types, the ability to vary heating rate or to operate isothermally at various temperatures during a program was considered essential. A schematic diagram of the first

device constructed in these laboratories which could maintain a constant low temperature for an extended length of time and which

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could be programmed from a very low temperature to room temperature and above in a linear and controllable manner is shown in Figure 1.

The unit utilizes compressed air, solid carbon dioxide, and an electrical heating element for obtaining temperatures as low as -70°C and for programming from this temperature to above ambient. The mode of operation is as follows. Compressed air from a laboratory bench line is dried in a molecular sieve and passes through a 3-way valve or stopcock. When cooling of the chromatography column is desired, the air is directed by the 3-way valve to a cooling compartment. The cooling compartment consists of two copper coils, 10 ft. x 0.25 in. o.d., arranged in parallel and surrounded by solid carbon dioxide. If starting temperatures lower than -78°C are needed, liquid nitrogen or other low temperature coolants may be used in the cooling compartment. Cold air flows into the chromatography column chamber, a copper box approximately 6 in. x 6 in. x 8 in., insulated with $1\frac{1}{2}$ in. of polystyrene or polyurethane foam. The temperature of the chamber is measured by a thermometer or thermocouple and can be controlled by allowing cold air to enter until the desired low temperature is reached. The column chamber is insulated well enough to maintain a constant low temperature for a considerable length of time. If the temperature rises slightly, more cold air may be admitted.

When it is desired to program the temperature of a column from a specified subambient temperature, the starting temperature is first established by means of the cooling air stream and held for several minutes. A sample is then injected onto the column. The cold air flow is shut off and warm air allowed to enter the column chamber by simply turning the 3-way valve. Air coming from the drying tube is now directed through an electrical heating element instead of through the cooling compartment. Hence, warm air enters the column chamber. Control of column temperature is maintained by adjusting the flow of warm air. By means of previously obtained calibration data it is possible to establish definite programs of temperature rise from the flow

rate. Knowing the power input to the electrical heating element and the air flow rate, reproducible temperature programs may be maintained. Programming may be linear or nonlinear as desired.

Temperature programming rates of $1\text{--}2^{\circ}\text{C}$ per minute to $8\text{--}10^{\circ}\text{C}$ per minute can easily be maintained by

the instrument. The control of air flow and heat is maintained manually. Figure 2 illustrates the reproducibility and linearity of a temperature program having a rise rate of 4°C per minute. One plot represents a starting temperature of -65°C , the other represents a starting temperature of -56°C .

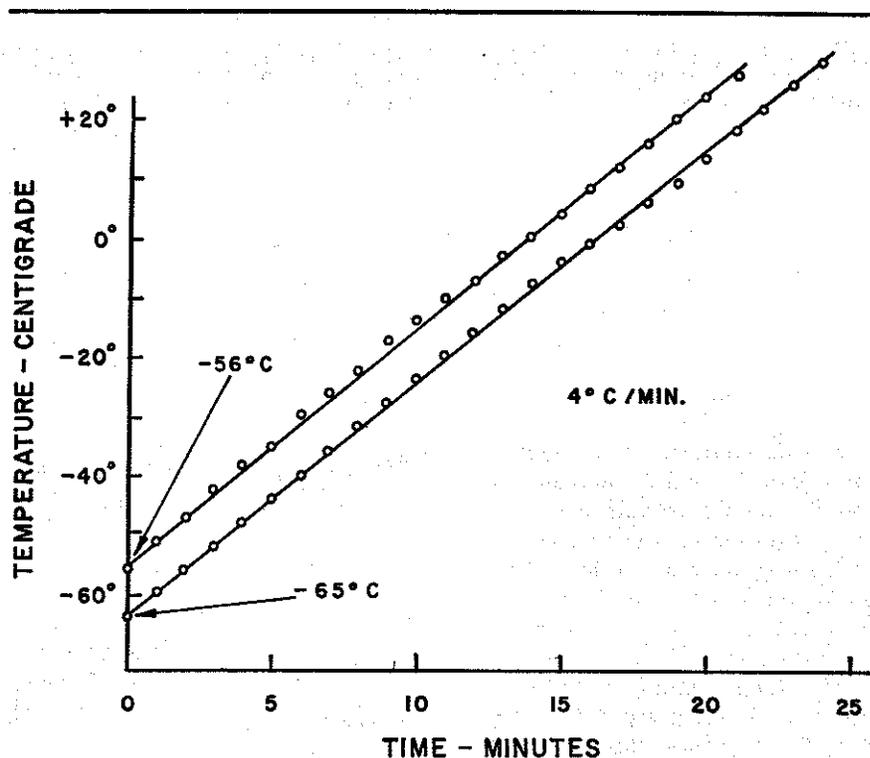


Figure 2. Graph of cryogenic temperature programs obtained with mixed air stream apparatus.

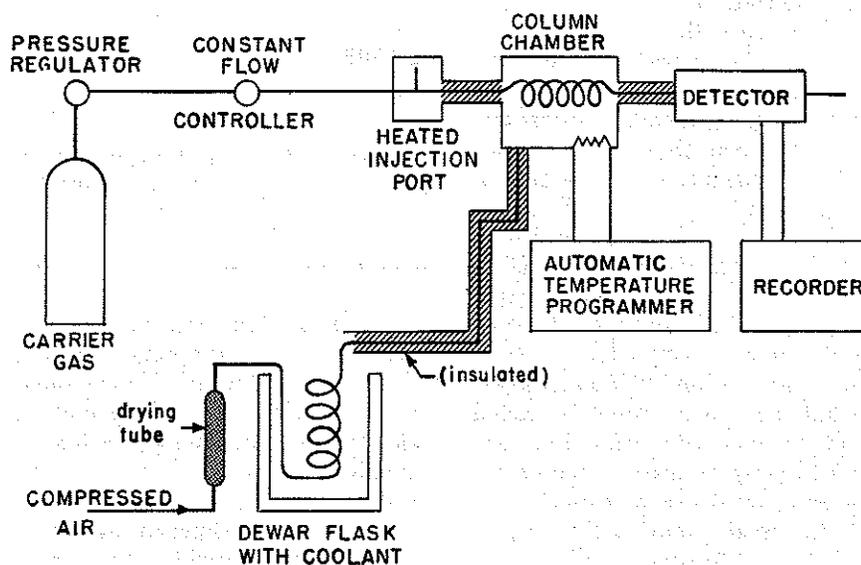


Figure 3. Diagram of programmed cryogenic temperature gas chromatography apparatus employing a cooled air stream with a conventional column chamber.

The final temperature of both was $+30^{\circ}\text{C}$. Each program ran for approximately twenty-four minutes and required only three adjustments of the controls. The adjustments were a change of voltage setting after seven minutes, another after sixteen minutes, and an air flow adjustment after nineteen minutes. Manual control is very simple once the instrument settings have been established for a particular programming rate. Excellent reproducibility is easily achieved. The chromatography column can be cooled from $+30^{\circ}\text{C}$ to -65°C in approximately fifteen minutes. The apparatus has been used successfully with both ionization and thermal conductivity detectors. The incorporation of a heating element within the column chamber would be desirable to enable programming to above ambient temperature, to provide for faster heating rates or for the purpose of purging columns after performing in the cryogenic temperature range.

Commercial gas chromatography equipment may be adapted for cryogenic programming if an automatic program controller is available to operate in the subambient range. A schematic diagram for modified commercial gas chromatography apparatus capable of programming the column temperature over a wide range is shown in Figure 3. The column chamber may be cooled very easily by blowing compressed air through a suitable coolant contained in a Dewar flask. This method has been found to work quite well when either dry ice-ethanol or liquid nitrogen coolant is used. Recently, it has been found that it is much simpler in most cases to employ dry ice or liquid nitrogen directly to cool the column chamber.

There are a few special precautions in operating procedure when using a wide-range temperature programmed gas chromatography apparatus. The injection port should be heated so that the sample is carried onto the column in the gaseous state and condensed as a slug on the head of the cold column or a system for direct on-column injection must be provided. The detector should be located in a separate compartment and sufficiently well insulated from the column chamber so that the effects of the changes in temperature of the col-

umn chamber are not transferred to the detector. The apparatus should include a flow controller, since, otherwise the carrier gas flow rate will vary greatly as the temperature varies. Column oven design requires special consideration. The use of both heater and cooling material in the same oven requires a well stirred air bath and careful selection of coolant location and column configuration to minimize undesirable temperature gradients.

Several commercial gas chromatographs have been successfully employed for cryogenic temperature programming. The column chamber of the F & M Scientific Company Model 720 gas chromatograph may be cooled by placing a small perforated tray of powdered dry ice on top of the heater coil protector cage. The F & M Scientific Company Model 1609 Gas Chromatograph may also be employed in a similar manner. The Aerograph Model 550B Hy-Fi Column Oven has been found particularly suitable for use with cryogenic programming employing liquid nitrogen as the coolant. A column chamber has recently been designed by the Barber-Colman Company which can be very conveniently cooled by means of liquid carbon dioxide pumped into the column chamber from a siphon tank. This apparatus may be used at temperatures in the liquid nitrogen range by introducing liquid nitrogen directly into the column chamber instead of the liquid carbon dioxide.

Automatic temperature programming devices are available which may be used to provide a variety of temperature programs. A power proportioning controller is required to insure accurate tracking of the selected temperature program over a wide range of initial temperatures and heating rates. Power output adequate to heat an oven containing an excess of cryogenic cooling material is required. Any power proportioning type of controller whose reference point can be set to a value in the subambient range should be capable of being used for cryogenic programming. Three such devices have been employed in these laboratories. The Barber-Colman Company has two models of programmers which have been specifically designed for operation in the subambient range and the F&M Model

240 Power Proportioning Programmer is very easily modified to employ a thermocouple reference junction at -78°C in dry ice, or even at -196°C in liquid nitrogen, though linear programs are not possible with the -196°C reference.

Modification of the F&M Model 240 programmer unit for low temperature use consists of a replacement of the 10K temperature compensating thermistor on the printed circuit board with a fixed 10K resistor (Figure 4). A reference thermocouple is connected in series with the sensing thermocouple. The latter is located in the column chamber; the former is immersed in an appropriate cryogenic reference bath contained in a Dewar flask.

Figure 5 shows some typical time-temperature plots for linear programs obtained with the Model 240 programmer. These data were obtained on an F&M Model 720 gas chromatograph whose column chamber was initially cooled below the starting temperature with powdered dry ice placed inside. A saturated solid carbon dioxide-ethanol bath at -78°C was employed as the cryogenic reference.

Millivolt readings were taken on a high sensitivity potentiometer (precise to 0.01 mv.) and converted to corresponding values of temperature of an iron-constantan thermocouple. The readings were made every minute until a temperature of 200°C was attained. The plots of these data (Figure 5) showed excellent linearity with each of the heating rates employed; namely, 3, 10, and 15°C per minute. At programming rates less than $3^{\circ}\text{C}/\text{minute}$, a slight non-linearity is observed due mainly to inability of the oven to maintain cryogenic temperatures for long periods of time, since at the very slow program rates natural warming of the oven causes the temperature to rise at a faster rate than would be due to the heat-input of the programmer. Although lower programming rates have been employed in cryogenic investigations conducted in these laboratories, they have been non-linear programs based on natural warming of an uninsulated column chamber. The dramatic improvement in separation effected by starting a program from a cryogenic range generally does not require use of linear rates less than $3^{\circ}\text{C}/\text{minute}$.

If it should be necessary to employ rates lower than 3°C/minute a more efficient insulation must be introduced.

If sufficient dry ice is placed in the column chamber in the initial

cooling operation, there will be solid remaining at the end of the program. This condition provides linear temperature programs, whereas when the dry ice was completely sublimed at the end of the program

there is occasionally some departure from linearity.

In the normal set-up of the instrument the reference is adjusted to ambient temperature. Consequently, with a -78°C reference, indicated pyrometer readings must be corrected to give actual values. In the case of the present work the actual temperature is the pyrometer reading less 103° [-78° - (+25°)]. During the course of a program, relative readings are taken from the pyrometer and converted, prior to plotting the data, to true temperatures.

A very low reference junction for the controller may be obtained by placing a thermocouple in liquid nitrogen. The programmer cannot produce, however, a controlled linear program because of the non-linearity of the response of thermocouples in this temperature range. With the apparatus employed in these laboratories, spontaneous temperature rise characteristics of the column chambers usually show a linear rise of about 3 to 5°C/minute from -180°C to -70°C so that there is little need for automatic programming in the very low temperature range. In any event, there is no special requirement for a linear rise characteristic for the separations sought at these temperatures. Programmed cryogenic temperature gas chromatography may now be performed with a variety of conveniently devised assemblies of apparatus. Conditions of operation may be varied to include linear or non-linear temperature programming from -196°C to over 200°C, and heating rates from 0.5°C to over 30°C per minute.

Acknowledgement

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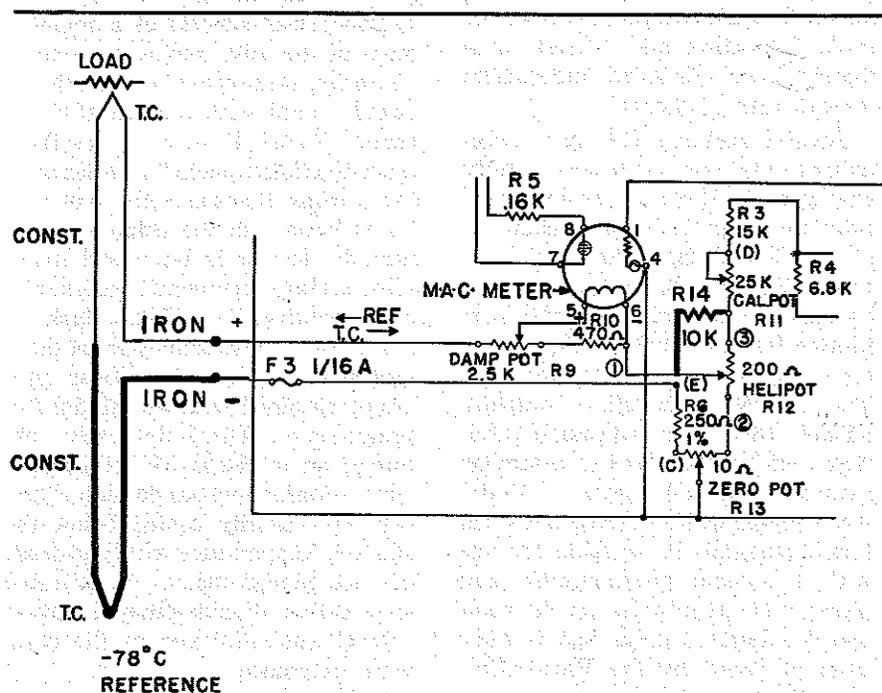


Figure 4. Section of circuit diagram for F&M Model 240 Linear Temperature Programmer showing modification for cryogenic starting temperatures. The heavy lines indicate the addition of the reference thermocouple and the replacement of the 10 K Ω thermistor with a 10 K Ω resistor.

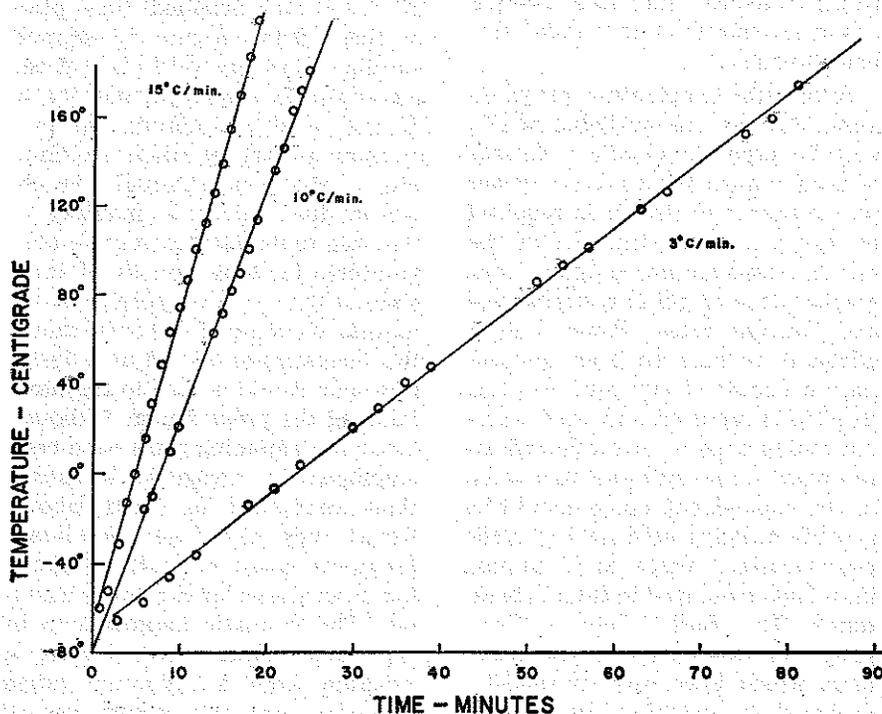


Figure 5. Graph of typical cryogenic temperature programs produced with an automatic programmer.