

A Gas Chromatographic Method for Analyzing Mixtures of Hydrocarbon and Inorganic Gases

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Abstract

Gas samples containing oxygen, nitrogen, hydrogen, helium, carbon dioxide, methane, and trace amounts of C₂ to C₅ hydrocarbons are analyzed by a gas chromatographic method that utilizes both thermal conductivity and flame ionization detectors. Porapak and molecular sieve columns are used with argon as the carrier gas. A column selector valve makes it possible to perform a complete analysis either on one 1 ml sample in 40 minutes, or on two 1 ml samples in 20 minutes. Samples are introduced either by on-column injection or through a gas sampling valve. By varying operational parameters, the speed, sensitivity, and accuracy of analysis may be modified.

Introduction

The geochemical study of the gases associated with peat and coal calls for the analysis of mixtures of hydrocarbon and inorganic gases. Gas samples generally contain CH₄, small amounts of C₂ to C₅ hydrocarbons, H₂, He, O₂, N₂, CO₂, and possibly water vapor. The amount of sample available for analysis varies from 1 to 200 ml.

Several gas chromatographic methods for the analysis of similar mixtures have been published. Doran and Cross (1) used a stream splitter and thermal conductivity detector with molecular sieve and Chromosorb P columns to analyze a single sample for O₂, N₂, CH₄, CO, CO₂, C₂H₆, C₃H₈, and n-C₄H₁₀. A three-column system with dual thermal conductivity detectors was used by Terry and Futrell (2) for analyses of C₂ to C₆ hydrocarbons with O₂ and N₂. Another three-column system with thermal conductivity detectors and hydrogen as the carrier gas was used to separate air, CO₂, H₂S, CH₄ and C₂ to C₄ hydrocarbons (3). A technique involving backflushing was used with Porapak and molecular sieve columns to analyze gas effluent for H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, and C₂H₂ in the presence of C₃ and heavier compounds (4). Combinations of Porapak and molecular sieve columns with thermal conductivity detectors were also used for the analysis of nitrous oxides and water in mixtures of hydrocarbons and fixed gases (5, 6). Since none of these methods was directly applicable to the gas mixture encountered, a method using three columns and thermal conductivity and flame ionization detectors was developed.

Experimental

A Micro-Tek 2000 R* gas chromatograph equipped

with thermal conductivity (TC) and dual flame ionization detectors (FID), a column selector valve, and a gas sampling valve is used (Figure 1). Three flow controllers are used to regulate carrier gas flow. A Varian dual channel recorder with dual disc integrators and printers records signals from both detectors simultaneously.

The three columns used are described in Table 1.

Effluent from column 1 passes through the column selector valve, going either to side 1 of the thermal conductivity detector, or to column 3 which leads to the flame ionization detector. Column 2 leads from side 1 to side 2 of the thermal conductivity detector. By

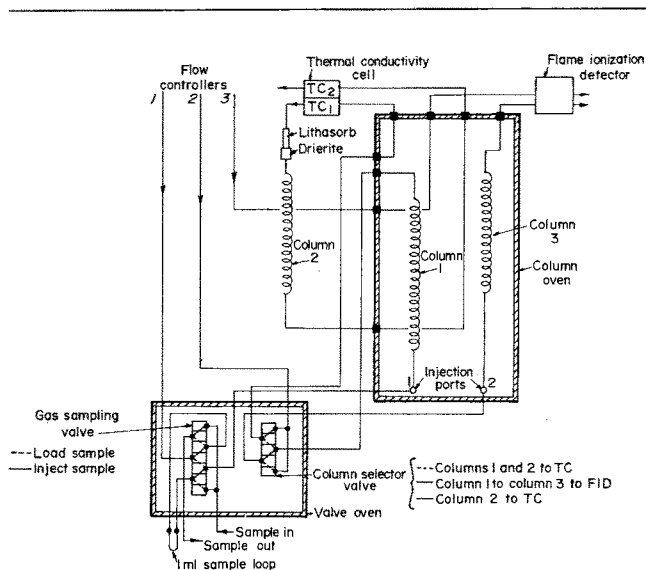


Figure 1. Diagram of gas chromatograph.

*Reference to trade names is for identification only and does not imply endorsement by the Bureau of Mines.

1. Doran, T. and Cross, J. P., *J. Gas Chromatog.*, **1966**, 260.
2. Terry, J. O. and Futrell, J. H., *Anal. Chem.*, **37**, 1165 (1965).
3. Malan, E. and Brink, B., *Chromatographia* **4**, 178 (1971).
4. Marchio, J. L., *J. Chromatog. Sci.*, **9**, 432 (1971).
5. Bennett, D., *J. Chromatog.*, **26**, 482 (1967).
6. Forsey, R. R., *J. Gas Chromatog.*, **1968**, 555.

reversing polarity, positive peaks are obtained from both sides of the TC. Carbon dioxide and water are removed from the gas before it reaches the molecular sieve column by two adsorption tubes; one with 60/80 mesh Lithasorb, the other with 60/80 mesh Drierite. The tubes connect side 1 of the TC to column 2. To reduce dead volume, all connections between columns, valves, and detectors are made with 1/16-in. stainless steel tubing.

Samples can be introduced into columns 1 or 3 either through the gas sampling valve or by on-column injection. Since hydrogen, helium, and nitrogen are sample components, argon is used as the carrier gas. The flow rate measured at both the TC outlet and the FID is 50 ml/min; delivery pressure is 80 psi. The use of argon limits the filament current to 100 ma at 155°C. The column oven temperature is held initially at 70°C, then programmed to 130°C. The second column is outside the chromatograph in a Dewar flask at 25°C. The temperature of the inlet oven is 110°C and the valve oven 135°C.

Analysis

If only a small amount of sample is available, a complete analysis can be performed with 1 ml of gas (Figure 2). The sample is injected on to column 1. Air, methane, and carbon dioxide are eluted from the first column and detected by side 1 of the thermal conductivity detector. Immediately after the CO₂ peak, the column selector valve is depressed and the C₂ to C₅ hydrocarbons pass from column 1 to column 3 and then to the flame ionization detector. The molecular sieve column separates helium, hydrogen, oxygen, and nitrogen which, with methane, are detected by side 2 of the thermal conductivity detector. Carbon monoxide, if present, elutes from column 2 after methane.

If enough gas is available, the analysis time is less if two samples are used (Figure 3). The first sample is injected on to column 1 for the determination of the inorganic gases; the concentrations of higher hydrocarbons are usually too small to be detected by the TC. After 3 minutes, another sample is injected on column 3 for hydrocarbon gas analysis. The same procedure is used if the sample is introduced through the gas sampling valve.

In both one and two sample methods, complete separation of methane, ethylene, ethane, normal and isobutane is obtained. The resolution of propane and propylene and the C₅ isomers depends upon total column length, rate and time of temperature programming. The butenes also can be determined by this method. Water vapor is not determined, but allowed to pass undetected through the flame ionization detector with the hydrocarbons.

The composition of the gas sample is calculated either by using relative response factors from the literature (7,8) or calibration factors determined from a standard sample. With the flame ionization detector, hydrocarbons can be determined quantitatively to .01 ppm and qualitatively at the ppb level. Gases detected by the thermal conductivity detector are calculated to .01 percent. By varying operational parameters, the

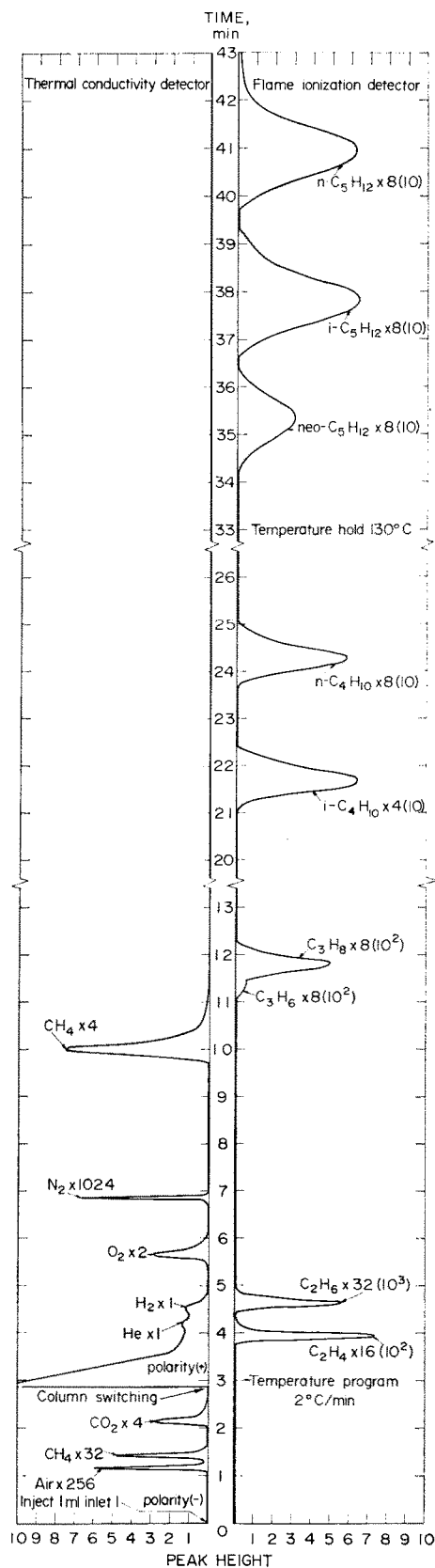


Figure 2. Chromatogram of single sample analysis.

7. Dietz, W. A., *J. Gas Chromatog.*, **1967**, 68.
8. Messner, A. E., Rosie, D. M., and Argabright, P. A., *Anal. Chem.*, **31**, 230 (1959).

Table I. Chromatographic Columns

Number	Column Packing	Length (feet)	Diameter (inches)	Packing preconditioning	Column conditioning
1	Porapak S Porapak T	12 3	1/8 1/8	Heated to 100°C in helium flow overnight	Heated at 150°C in argon flow overnight
2	Molecular sieve 13x	20	1/4	—	Heated to 300°C in vacuum overnight
3	Porapak Q	9.5	1/8	Heated to 100°C in helium flow overnight	Heated to 150°C in argon flow overnight

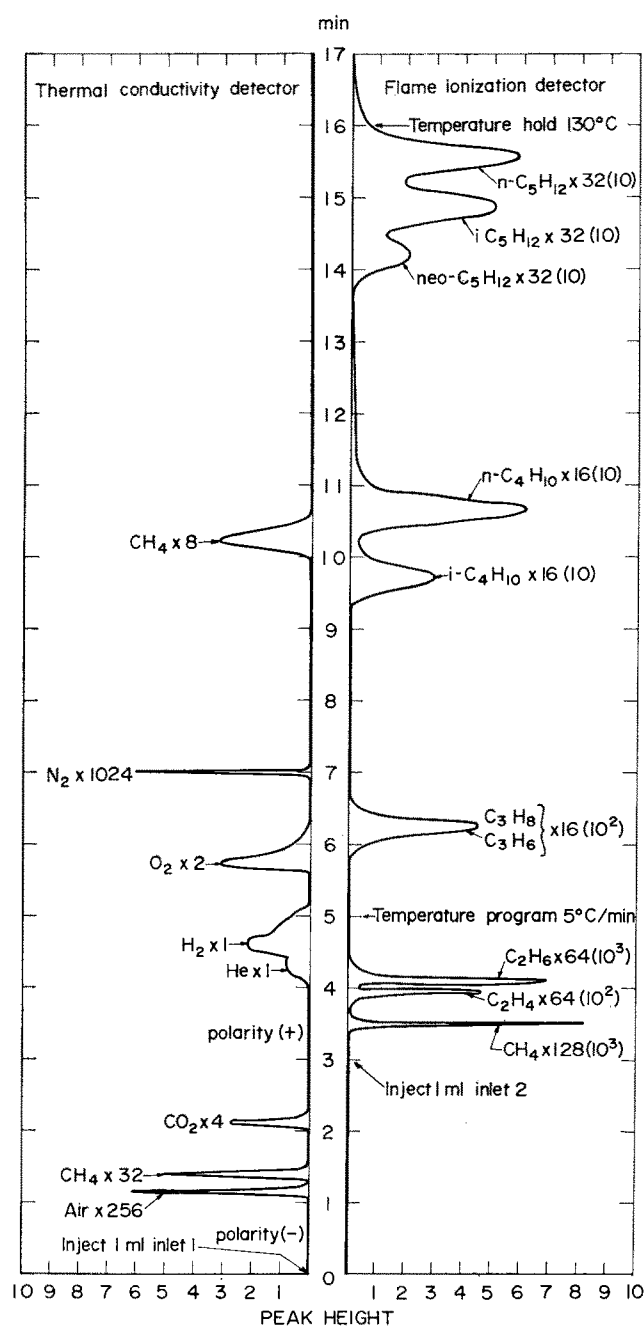


Figure 3. Chromatogram of two sample analysis.

method can be modified to provide the speed, sensitivity, degree of resolution and accuracy needed for a particular analysis.

The method has been used to analyze gases produced during microbial decomposition of plant material, gases desorbed from peat and coal, coal-bed gases and hydrocarbons dissolved in water.

Summary

A simple gas chromatographic method has been developed for analyzing complex mixtures of hydrocarbon and inorganic gases; it is versatile, sensitive, and readily adapted to different types of samples, varying in size and composition. Inorganic gases and methane are detected by a thermal conductivity detector; a flame ionization detector is sensitive to CH₄ and to trace amounts of the C₂ through C₅ hydrocarbons. A complete analysis can be performed on samples as small as 1 ml. A single sample analysis can be completed in 40 minutes. If sufficient gas is available for two samples, the analysis can be completed in less than 20 minutes. ■

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