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Note

One-step analysis of a mixture of permanent gases and light hydrocarbons by gas chromatography

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Mixtures of permanent gases and light hydrocarbons are usually encountered in petrochemical systems that involve cracking, steam reforming, partial combustion, etc. The complete analysis of such mixtures by gas chromatography with a single sample injection still remains a problem.

Various methods involving the use of combinations of multiple columns, multiple detectors and multiple sample injections have been reported by Sevenster[1], Hobbs[2], Takamiya and Sukenaga[3], Trowell[4], Archer[5], Lo-Chang[6] and others, and these methods are usually very complicated. Cross[7] described a polymer column which separated hydrogen, carbon monoxide, methane, carbon dioxide, acetylene and ethane. Gornak and Komarov[8] reported that natural glauconite was an excellent adsorbent for the separation and analysis of mixtures of hydrogen, air, carbon dioxide and C_1–C_{12} hydrocarbons using helium as the carrier gas. A mixture of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide and C_1–C_4 hydrocarbons was separated[9] by using a single column (Poropak Q), a single sample injection and a single detector system with temperature programming from $-65°$ to $+200°$, and with helium as the carrier gas.

This paper describes the development of an analytical technique for mixtures of permanent gases and light hydrocarbons with a single sample injection using hydrogen as the carrier gas and without the use of any sub-ambient temperature programming. This technique is somewhat similar to those reported by Madison[10] and Cvejanovich[11], but is simpler and less complicated.

EXPERIMENTAL AND RESULTS

A Perkin-Elmer (Model 900) chromatograph was modified as shown in the flow diagram in Fig. 1. Two standard Poropak Q columns were fitted inside the programmed oven of the dual column chromatograph; the outlet of one of the columns was divided into two lines through a gas sampling valve (Pye 104), one passing through a molecular sieve 5A column maintained at 55° in a box with a hot-air blower and the other passing through a needle valve in order to keep the pressure drop through two lines the same. Both of these lines were then connected through a T-piece to the thermal conductivity detector.

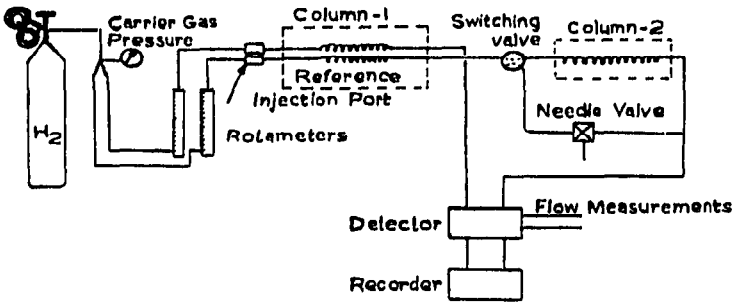

Fig. 1. Flow diagram of chromatographic system.

Initially, the Poropak and the molecular sieve columns were arranged in series, and nitrogen, oxygen, methane and carbon monoxide were allowed to leave the first column (50°) and enter the second. Then the molecular sieve was by-passed and carbon dioxide and hydrocarbons were allowed to leave the first column with temperature programming and pass into the detector. Subsequently, the effluent from the first column was again allowed to pass through the molecular sieve so as to separate nitrogen, oxygen, methane and carbon monoxide. The time required for a complete analysis was about 30 min.

Fig. 2 shows the recorder response for the analysis of a mixture of nitrogen,

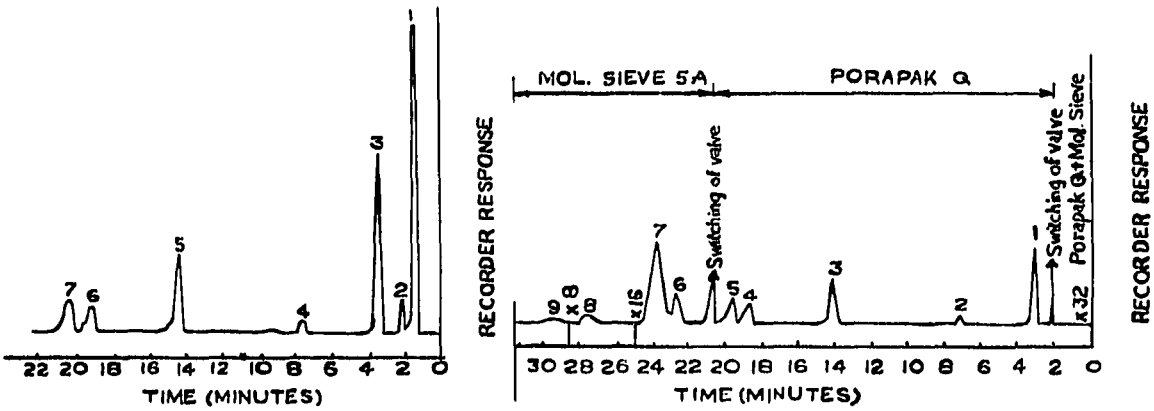

Fig. 2. Chromatography of a mixture of nitrogen, oxygen, methane, carbon monoxide and LPG using the Porapak Q column alone. Column: 6 ft. × 1/4 in. O.D. stainless steel. Column packing: Poropak Q. Carrier gas: hydrogen, flow-rate 40 ml/min. Temperature programme: initial by 50° for 3 min, increasing at 8°/min to 150°. Detector: thermal conductivity, temperature 150°; bridge current 100 mA. Peaks: 1= air; 2= methane+carbon monoxide; 3= carbon dioxide; 4= ethane; 5= propane; 6= isobutane; 7= *n*-butane.

Fig. 3. Chromatography of the same mixture as in Fig. 2 using the present technique. Column 1: 6 ft. × 1/4 in. O.D. stainless steel, Porapak Q. Column 2: 10 ft. × 1/4 in. O.D. copper, 30–60 mesh molecular sieve 5A. Carrier gas: hydrogen, flow-rate 40 ml/min. Temperature programme: column 1, initially 50° for 3 min, increasing at 8°/min to 150°; column 2, isothermal (55°). Detector: thermal conductivity, temperature 150°; bridge current 100 mA. Peaks: 1= carbon dioxide; 2= ethane; 3= propane; 4= isobutane; 5= *n*-butane; 6= oxygen; 7= nitrogen; 8= methane; 9= carbon monoxide.

oxygen, methane, carbon monoxide and liquefied petroleum gas (LPG) (containing ethane, propane, *n*-butane and isobutane) using the Poropak Q column alone. Fig. 3 shows the analysis of the same mixture using the present technique.

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