

Short Communications

The behavior of isobutane on a molecular sieve gas chromatography column

People who routinely use a Linde 5A molecular sieve gas chromatography column for the analysis of mixtures of permanent gases and light hydrocarbons occasionally find a shifting peak in their gas chromatograms where identification is not obvious. Such a peak may be due to the presence of isobutane. Using vapor pressure considerations only, one would expect the retention time of isobutane to be several times that of methane. Actually, there can be a certain column operating temperature where the retention volume of isobutane is the same as nitrogen. At another operating temperature, isobutane in the gas chromatogram comes out just barely beyond methane.

In an experiment to study the retention of isobutane on molecular sieve, we

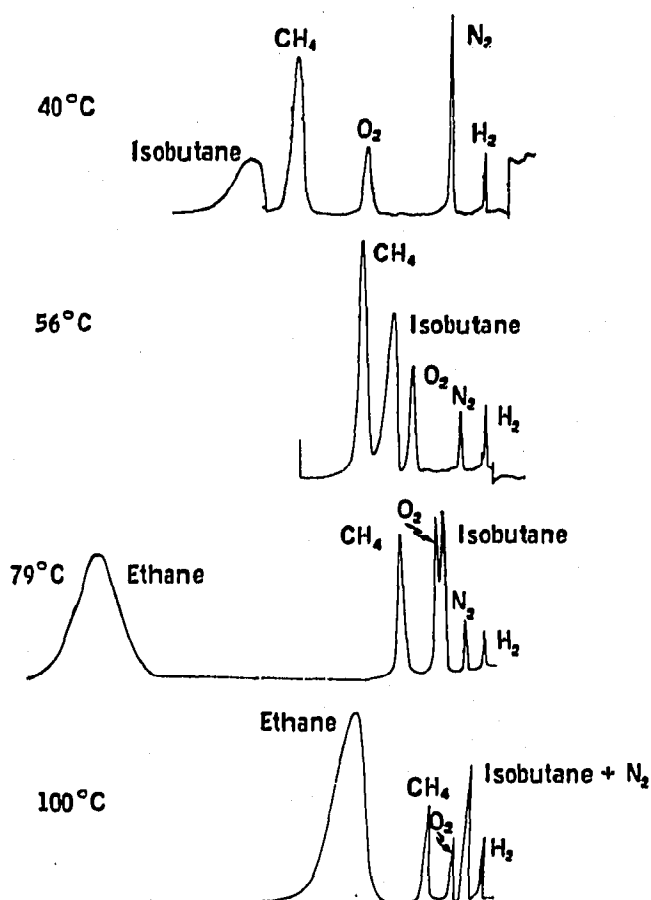


Fig. 1. Gas chromatograms at 4 different temperatures of a mixture of permanent gases and light hydrocarbons on a Linde 5A molecular sieve column.

separated a mixture of permanent gases and light hydrocarbons using a 10 ft. Linde 5A molecular sieve gas chromatography column. The gaseous mixture contained hydrogen, nitrogen, oxygen, methane, ethane, propane, isobutane, and *n*-butane. Separations were performed isothermally at 40°, 56°, 79°, and 100°. A mass spectrometer connected to the exit of the gas chromatograph¹ was used to identify each compound as it emerged from the column.

We see in Fig. 1 that isobutane is in a different spot in each gas chromatogram. It has a much smaller retention volume than either ethane, propane, or *n*-butane. Propane and *n*-butane were not observed in any of the chromatograms. Ethane was eventually eluted at 56° but was not observed at 40°. The relative retention volume of isobutane, relative to methane or any of the permanent gases, is observed to decrease as the operating temperature of the molecular sieve column increases.

Separations are made in a molecular sieve column by gas-solid chromatography coupled with a selective screening by the pores of the molecular sieve. An isobutane molecule has too large a critical diameter to pass through the screening pores; thus adsorption and desorption of isobutane can only occur on the external surface of the molecular sieve. This difference in surface areas, 1-3 m²/g for the external area versus 700-800 m²/g for the internal surface area², can account for the small retention volume of isobutane relative to the other compounds.

Because isobutane is seemingly adsorbed only on the external surface of the molecular sieve, its position in chromatograms is far more sensitive to flow rate, temperature, and previous column history than the permanent gases or small hydrocarbons which are adsorbed on the internal surface. If isobutane is present, care must be taken to see that it is not reported as one of the permanent gases.

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¹ L. P. LINDEMAN AND J. L. ANNIS, *Anal. Chem.*, 32 (1960) 1742.

² Linde Air Products Company, a Division of Union Carbide, *Technical Data Sheet*, No. 9947-A.

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