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Note

A column packing for the separation of permanent gases and light hydrocarbons by gas–solid chromatography

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In an earlier paper[1], a one-step separation of a mixture of permanent gases and light hydrocarbons by a chromatographic system with a two-column combination (Porapak Q and molecular sieve 5A) was reported. Further work was continued in order to achieve such a separation with a single chromatographic column and a simple temperature programme. In this paper, we report the development of a mixed column packing of silica gel–alumina which effects the desired separation on a single 10-ft column.

Green and Pust[2] studied the separation of oxygen, nitrogen, carbon monoxide and C_1–C_4 hydrocarbons on alumina and silica gels with temperature programming above ambient temperature. Kiselev *et al.*[3] studied a similar separation on Saran charcoal. Phillips and Scott[4] reviewed the use of modified alumina and silica gels for such separations. Horton[5] reported the separation of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide and C_1–C_3 hydrocarbons on molecular sieve 5A using isothermal conditions and temperature programmes above ambient temperature. Deans *et al.*[6] reported similar work on molecular sieve 13X. Cross[7] reported a polymer column that separated hydrogen, carbon monoxide, carbon dioxide and C_1 and C_2 hydrocarbons at 30°. Our experience has been that with a single column, permanent gases (with the exception of carbon dioxide) are best separated on molecular sieves (5A and 13X), and a mixture of permanent gases and light hydrocarbons are best separated on Porapak Q, with the disadvantage, however, that oxygen plus nitrogen and carbon monoxide plus methane appear as composite, unresolved peaks unless very low temperatures are used. It was this problem that led to the present search for a column packing material that would resolve all the components individually. Initially, it was intended to standardize a mixed silica–alumina gel so as to give the best separation possible, and then to modify it by deposition of suitable compounds in order to achieve the desired properties.

A systematic gas chromatographic study was made of the retention times of individual components with silica–alumina gels (prepared in the laboratory), the proportion of silica being 10, 25, 50, 75 and 100%. Then a mixture of oxygen, nitrogen, carbon monoxide, carbon dioxide, methane and an LPG containing ethane, propane, isobutane and butane was resolved in a 10-ft. long, ¼-in. O.D. copper column using

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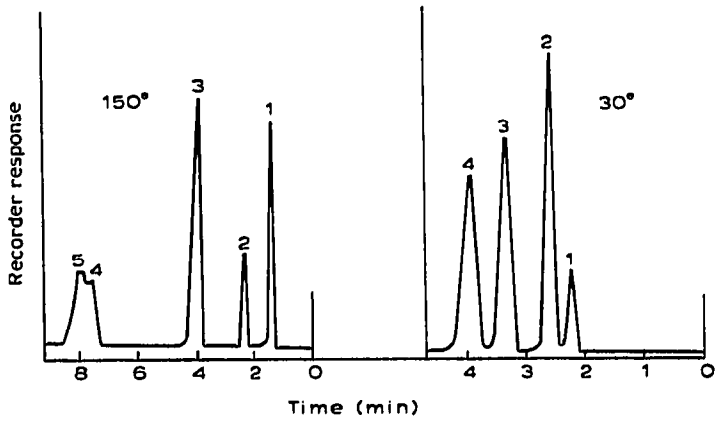

Fig. 1. Chromatogram with 50:50 silica–alumina gel as column packing. Peaks at 30°: 1, oxygen; 2, nitrogen; 3, methane; 4, carbon monoxide. Peaks at 150°: 1, oxygen, nitrogen, methane and carbon monoxide; 2, ethane; 3, propane; 4, isobutane; 5, *n*-butane.

two isothermal conditions, one at ambient temperature and another between 150° and 200°. A Pye 104 gas chromatograph with a thermal conductivity detector was used with hydrogen as the carrier gas at a flow-rate of 30 ml/min. The detector bridge current was kept at 100 mA. The best separation was obtained with the 50:50 gel, as shown in Fig. 1. At ambient temperature, oxygen, nitrogen, carbon monoxide and methane were resolved completely; carbon dioxide and higher hydrocarbons did not appear after 40 min. At the higher temperature, ethane, propane and butane were resolved; carbon dioxide did not appear after 40 min even at 200°.

The 50:50 mixed alumina–silica gel was modified by depositing on it 2.2% (w/w) of ammonium chromate. Fig. 2 shows the chromatograms obtained on this modified gel. All of the components were resolved satisfactorily, although with lower

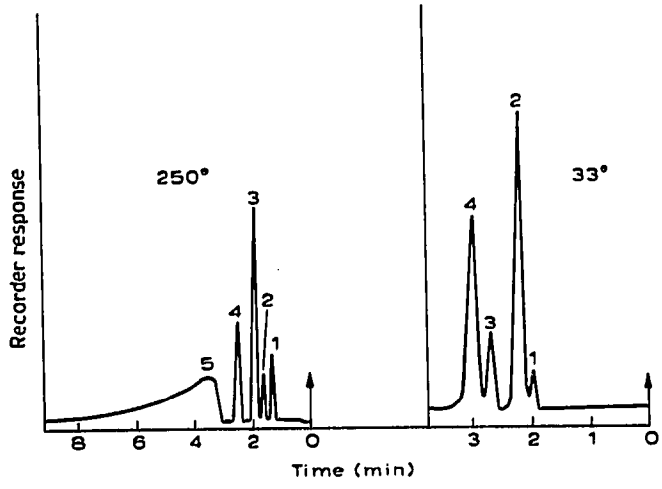

Fig. 2. Chromatogram with 50:50 silica–alumina gel modified with ammonium chromate as column packing. Peaks at 33°: 1, oxygen; 2, nitrogen; 3, methane; 4, carbon monoxide. Peaks at 250°: 1, oxygen, nitrogen, methane and carbon monoxide; 2, ethane; 3, propane; 4, butanes; 5, carbon dioxide.

retention times than with the original gel. A temperature of 250° was required in order to obtain a reasonable peak for carbon dioxide.

The results show that the 50:50 silica–alumina gel and its modified form are excellent packing materials for the separation of permanent gases and light hydrocarbons with a suitable temperature programming above ambient temperature. Silica gel was prepared by adding nitric acid to sodium silicate solution. The mixed gel was prepared by adding a calculated amount of sodium aluminate solution to wet silica gel and precipitating alumina gel by adding a concentrated solution of aluminium nitrate, with constant stirring, and adjusting the pH to 6. Several repetitive preparations were made at different ambient temperatures (25–33°). The gel was completely reproducible. For conditioning, the gel, after crushing and sizing, was heated at 500° for 2 h. After column packing, carrier gas was passed through the packing at 200° for 2 h before starting the analysis. For the modified gel, the finished and heat-treated particles were soaked in ammonium chromate solution and the mixture evaporated to dryness on a water-bath, followed by heating the dried solids for 2 h at 500°.

Further work is in progress to examine the possible application of the mixed gel in the analysis of other substances.

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