Notes

Analysis of gas mixtures by gas chromatography

A recent investigation by BENNETT[1] has shown that a gas mixture containing oxygen, nitrogen, methane, carbon dioxide and nitrous oxide can be successfully separated within nine minutes using both sides of a flow-through detector and a configuration employing two columns in series.

The disadvantages of this system are listed below:

(1) Peak polarity reversal is required.

(2) Insertion of a delay coil increases dead volume within the system.

(3) Carbon dioxide and nitrous oxide are irreversibly adsorbed on the second column (Molecular Sieve 5A), and this will shorten its useful life.

(4) The analysis time is increased by methane eluting from the second column although a methane peak suitable for measurement has already emerged from the first column.

(5) The separation between some of the peaks is not to baseline, and would possibly disappear if the ratios of these adjacent peaks were vastly different. To rectify this with the described configuration would lengthen analysis time.

The above disadvantages can all be overcome using a 6-port column switching valve and a peak parking technique. By use of columns of similar separating properties to those used by BENNETT[1], namely a pre-column of porous polymer beads and a parking column of molecular sieve, the complete separation to baseline of oxygen, nitrogen, methane, carbon dioxide and nitrous oxide can be achieved within five minutes.

Equipment

The column configuration used is shown in Fig. 1. Column 1 is 18 ft. × 0.1 in. I.D. (O.D. 1/8 in.) copper tubing filled with 50/80 mesh Porapak Q (Waters Associates Limited, Stockport, Cheshire). Column 2 is 6 ft. × 0.2 in. I.D. (O.D. 1/4 in.) copper tube filled with 36/44 mesh Molecular Sieve 13X previously activated by heating at 250° for 7 h under vacuum. Both columns operated at ambient temperatures. There is no significance in the columns being of different diameters, the choice was decided by availability. The carrier gas was helium at a flow of 75 cc per minute.

The 6-port valve used in our work is made by Sherbourne Engineering in the U.S.A. and marketed in the U.K. by M.S.A. Instrument Division, Queenslie Estate, Glasgow. This valve is a pneumatically actuated slide valve of the type used in process control gas chromatography, however, any 6-port valve either rotary or sliding, whether manually or pneumatically actuated can be used with the same result. The valve allows the configuration to be switched from Mode 1, where columns 1 and 2 are in series with the detector, to Mode 2, where column 1 is in series with a needle valve and the detector, column 2 being by-passed (Fig. 1).

The needle valve is set so that the flow through the detector is the same in both

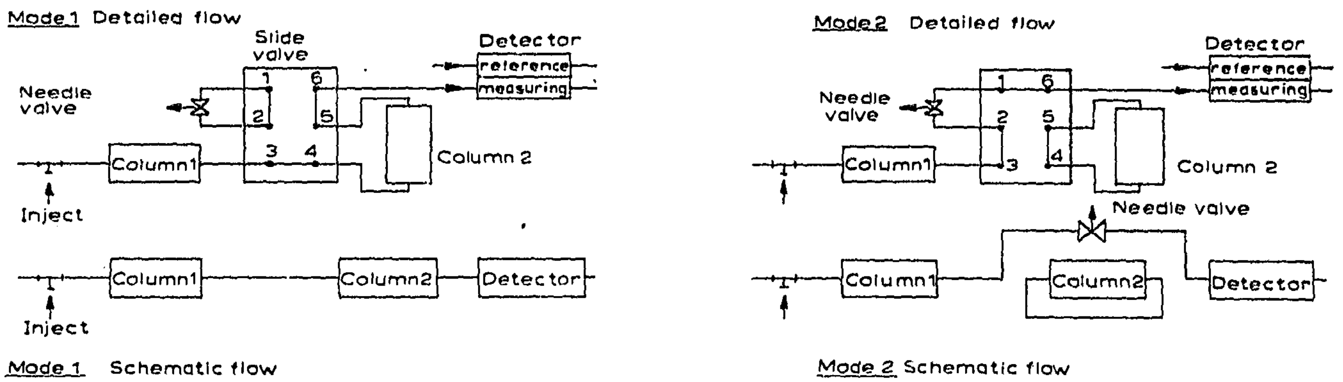

Fig. 1. Column configuration.

modes thus minimising baseline shift on switching modes. The needle valve used is a Nuclear Products type 1SA sold in the U.K. by Techmation Ltd., 19, Carlisle Road, Colindale, London, N.W. 9.

The detector used was a conventional flow-through type made by our own workshop, fitted with Fenwal Electronics Inc. Thermistors and operated at room

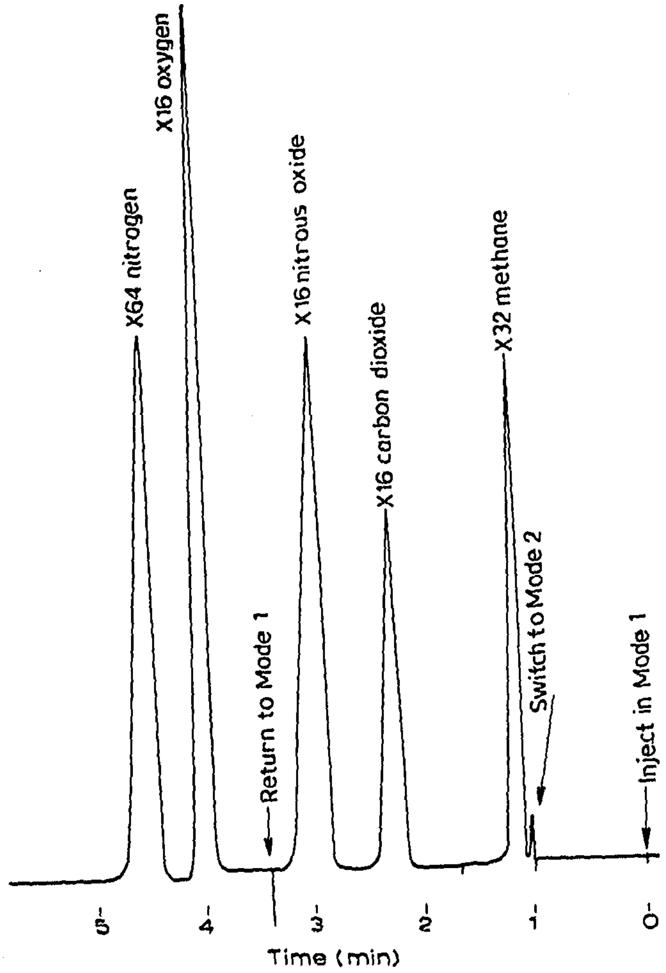

Fig. 2. Analysis of methane, carbon dioxide, nitrous oxide, oxygen and nitrogen by peak parking.

temperature. However, detectors with "cul-de-sac" reference cells could be used. The detector, columns, and valve were housed in an asbestos board oven to avoid draughts. The bridge unit, attenuator and voltage supply were assembled in modular form by our own workshop from commercially available components.

Experimental

Samples were introduced using a 1 ml gas syringe but, if preferred for quantitative work, introduction by a gas sampling valve is possible.

Initially, a sample of air was introduced with the columns in Mode 2 and the time for the composite oxygen/nitrogen peak to elute noted. The column configuration was then switched to Mode 1 and the sample injected. The first column separates the oxygen/nitrogen peak ahead of the remainder of the components and in this mode this peak enters the Molecular Sieve column after a time which can be deduced from the runs in Mode 2. Once the oxygen/nitrogen peak is timed to have entered column 2 and before methane, the second peak, has left column 1, the configuration is switched to Mode 2, thus parking the composite peak on column 2. Methane, carbon dioxide and nitrous oxide are then eluted directly from column 1 into the detector. Once nitrous oxide has emerged, the configuration is switched back to Mode 1 to allow oxygen and nitrogen to elute from column 2. All components are eluted within 5 min and are sufficiently separated to allow attenuation changes to be effected (Fig. 2).

Results

The total analysis time is 5 min, and the difficulties mentioned using both sides of the detector are overcome. No quantitative work was carried out on this stream, but a similar analysis is carried out in our laboratories using the peak parking technique. Injection in this case is achieved by flushing a fixed volume of sample at a known pressure into column 1. The average repeatability of peak areas measured on real analyses expressed as a % error at 95 % confidence limits is ± 3.3 %.

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1 D. BENNETT, *J. Chromatog.*, 26 (1967) 482.

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