Analysis of gas mixtures by gas chromatography

The purpose of this investigation was to develop a reproducible chromatographic technique for the quantitative analysis of gas mixtures containing oxygen, nitrogen, methane, nitrous oxide and carbon dioxide. The use of types 5A and 13X molecular sieves has been reported[1,2] for the separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide. GRAVEN[3] developed a method, using temperature programming, for the separation of mixtures containing oxygen, nitrogen, nitrous oxide, carbon dioxide, carbon monoxide and methane. MURAKAMI[4] has analysed a mixture containing oxygen, nitrogen, methane, carbon monoxide and carbon dioxide using an arrangement of two columns in series. The gases passed first through a silica gel column to the reference cell of a thermal conductivity detector, then through a molecular sieve column and finally through the measuring cell of the detector. By suitable switching of the recorder polarity a continuous chromatogram was obtained showing a peak for the mixture of oxygen, nitrogen, methane and carbon monoxide followed by a carbon dioxide peak from the silica gel column, then individual peaks of oxygen, nitrogen, methane and carbon monoxide from the molecular sieve column. A similar technique was used by MANKA[5] for the separation of hydrogen in addition to the other gases.

Nitrous oxide and carbon dioxide have until recently proved difficult to separate by gas chromatography. Separations have been reported on columns packed with silica gel[6], charcoal[7], molecular sieve[8] and dimethyl sulphoxide on Sil-o-cel[9] but acceptable chromatograms are difficult to obtain without careful pre-treatment of the column packings. HOLLIS[10] has demonstrated that nitrous oxide and carbon dioxide are readily separated on a column packed with porous beads of a polymer made from ethylvinylbenzene with divinylbenzene as crosslinker. The work described here uses two columns in series to effect complete separation of oxygen, nitrogen, methane, carbon dioxide and nitrous oxide; the first is packed with porous polymer beads and the second with 5A molecular sieve.

Experimental

A gas chromatographic system employing two columns in series is used for the analysis so that all the components can be determined in a single sample. A length of copper tubing between the columns enables the gases which are separated on column I to be eluted before any emerge from column II. This permits the use of one detector resulting in a continuous chromatogram with no peak overlap.

The apparatus is shown diagrammatically in Fig. 1.

Column I is a 2 ft. 3 in. length of 0.25 in. O.D. copper tubing filled with 50–80

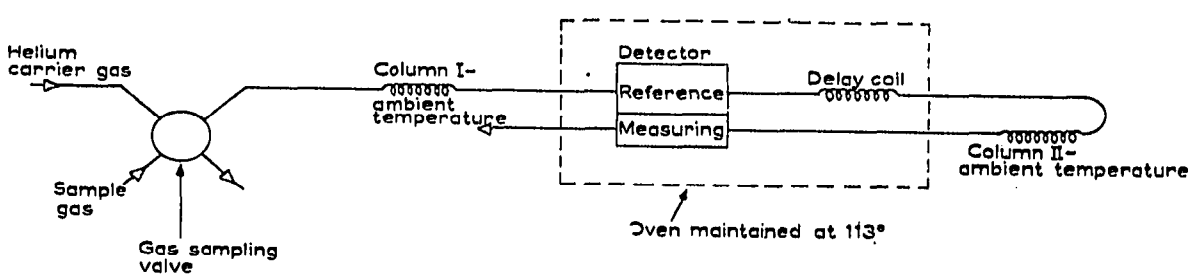

Fig. 1. Arrangement of columns.

mesh Porapak Q (Waters Associates Limited, Stockport, Ches.). This column is operated at ambient temperature.

The delay coil is a 7 ft. length of 0.125 in. O.D. copper tubing housed in the detector oven. All connections are made with compression couplings (Simplifix Limited, Maidenhead, Berks.).

Column II is a 6 ft. length of 0.25 in. O.D. copper tubing packed with 30–60 mesh 5A molecular sieve. The molecular sieve was activated prior to packing by heating at 250° for 4 h under vacuum. This column is also operated at ambient temperature.

A Gow Mac type 9285 thermal conductivity cell fitted with SS/W2 filaments was used in conjunction with a Gas Chromatography Limited RY 100 bridge unit. The detector was maintained at 113° in a Griffin and George Limited precision air thermostat oven. The bridge output was recorded on a Sunvic 0–5 mV potentiometric recorder. Helium was used as carrier gas at a flowrate of 50 ml/min.

The column arrangement uses the reference cell of the katharometer to detect gases from column I and the measuring cell to detect gases from column II. Peaks from either cell can be recorded in a continuous chromatogram by reversing the polarity of the detector signal. To achieve this without affecting the base line the recorder input signal is first adjusted to zero potential.

Samples were introduced into the chromatograph using a Perkin Elmer gas valve. Column I gives a peak representing the mixture of oxygen and nitrogen followed by individual peaks for methane, carbon dioxide and nitrous oxide. From the reference cell the gases pass on to column II which gives individual peaks for oxygen

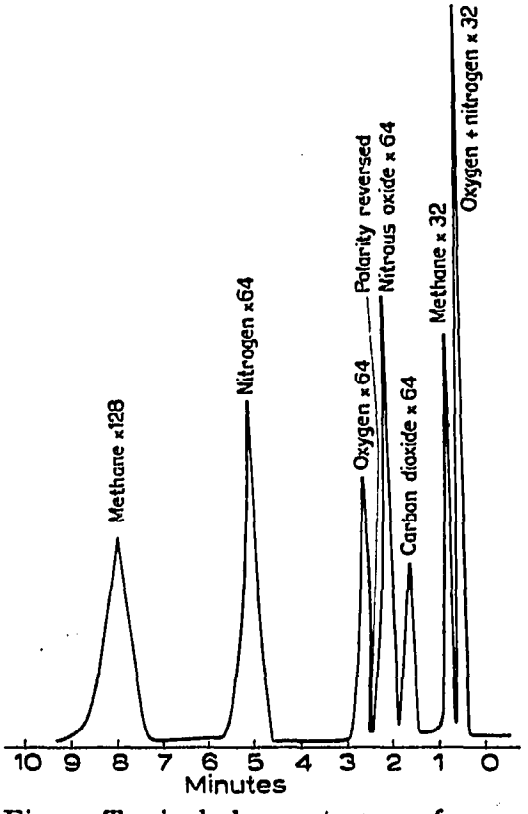

Fig. 2. Typical chromatogram for sample of gas mixture.

nitrogen and methane. Carbon dioxide and nitrous oxide are irreversibly adsorbed on this column.

Results

A typical chromatogram is shown in Fig. 2. The precision of the method was assessed by introducing twelve 1.1 ml samples of the individual gases into the chromatograph. The resulting peak areas, measured by a triangulation method, are shown in Table I.

TABLE I

PEAK AREAS FOR DUPLICATE SAMPLES OF INDIVIDUAL GASES

Helium flowrate: 50 ml/min. Sample size: 1.1 ml at N.T.P. Bridge current: 250 mA. Sensitivity corrected to × 1. Chart speed: 30 in./h. Detector temperature: 113°. Column temperature ambient.

Gas sample No.	*Methane (Porapak)*	*Methane (Molecular sieve)*	*Carbon dioxide*	*Nitrous oxide*	*Oxygen*	*Nitrogen*
1	0.291	0.277	0.304	0.418	0.288	0.328
2	0.290	0.277	0.304	0.419	0.288	0.329
3	0.291	0.277	0.305	0.419	0.288	0.324
4	0.289	0.275	0.304	0.414	0.282	0.323
5	0.290	0.277	0.306	0.418	0.282	0.321
6	0.290	0.278	0.308	0.405	0.281	0.318
7	0.291	0.275	0.304	0.417	0.281	0.324
8	0.289	0.273	0.305	0.417	0.288	0.323
9	0.289	0.277	0.304	0.414	0.288	0.321
10	0.290	0.278	0.304	0.415	0.283	0.319
11	0.289	0.276	0.306	0.423	0.283	0.321
12	0.290	0.278	0.303	0.416	0.288	0.321
Mean	0.290	0.277	0.305	0.416	0.285	0.324
σ	0.0005	0.0014	0.0015	0.004	0.0005	0.0025
Cv	0.175%	0.506%	0.498%	0.973%	0.175%	0.787%

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1 G. KYRYACOS AND C. E. BOORD, *Anal. Chem.*, 29 (1957) 787.
2 J. F. ELLIS AND C. W. FORREST, *Anal. Chim. Acta*, 24 (1961) 329.
3 W. M. GRAVEN, *Anal. Chem.*, 31 (1959) 1197.
4 Y. MURAKAMI, *Bull. Chem. Soc. Japan*, 32 (1959) 316.
5 D. P. MANKA, *Anal. Chem.*, 36 (1964) 480.
6 L. MARVILLET AND J. TRANCHANT, *Proc. Symp. Gas Chromatog., 3rd, Edinburgh, 1960*, p. 321.
7 D. H. SMITH AND F. E. CLARK, *Soil Sci. Soc. Am. Proc.*, 24 (1960) 111.
8 R. P. DEGRAZIO, *J. Gas Chromatog.*, 3 (1965) 204.
9 E. R. ADLARD AND D. W. HILL, *Nature*, 186 (1960) 1045.
10 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.

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