

CHROMSYMP. 192

GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBONS UP TO C₁₆ AND OF INERT GASES IN NATURAL GAS WITH A COMBINATION OF PACKED AND CAPILLARY COLUMNS

L. HUBER* and H. OBBENS

Hewlett-Packard GmbH, P.O. Box 1280, 7517 Waldbronn (F.R.G.)

SUMMARY

A gaschromatographic method is described, which gives quantitative information on hydrocarbons and inert gases in natural gas in a single run. Inert gases and hydrocarbons up to C₂ are separated on a combination of Porapak and molecular sieve columns. For the separation of the higher hydrocarbons, a methylsilicone capillary column with a thick film was used. The method is suitable for routine laboratory analysis and automated on-line monitoring.

INTRODUCTION

Several gas chromatographic (GC) methods have been developed for analysing natural gas and condensates¹⁻⁸, all of which were suitable for analysing either light components and hydrocarbons up to C₈ or only hydrocarbons up to C₁₆. The GC system described here permits the analysis of both inert gases and hydrocarbons up to C₁₆ with a single gas chromatograph.

EXPERIMENTAL

The GC system consists of a Hewlett-Packard 5880A gas chromatograph with a flame-ionization detector, a capillary column for hydrocarbons analysis, a thermal conductivity detector and two packed columns for the analysis of the inert gases. A diagram of the chromatographic system is shown in Fig. 1. Two gas sampling valves and one column isolation valve, all automatically controlled, are installed in a thermostatically controlled heated compartment.

Separation of oxygen, nitrogen and methane is achieved on a molecular sieve 13X column. Ethane and carbon dioxide are separated on a combined Porapak T and Porapak Q column. The hydrocarbon separation is obtained on a 50 m × 0.2-mm I.D. fused-silica capillary column, coated with a 0.5- μ m film of cross-linked methylsilicone gum. The thick film permits the separation of gas components without requiring cryogenic cooling of the column oven. The capillary injection system is directly connected to a six-port gas sampling valve.

A BASIC program controls the entire analysis sequence and also carries out

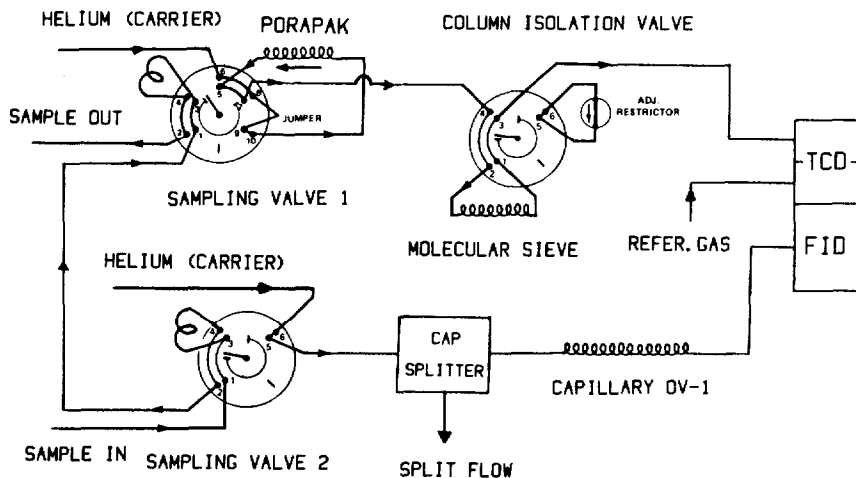


Fig. 1. Schematic diagram of the chromatographic system. TCD = Thermal conductivity detector; FID = flame-ionization detector.

post-chromatographic calculations, *e.g.*, calorific value, specific gravity and the Wobbe index*. Alternatively, a data communications interface can be used to transmit the chromatographic reports to an external computer, which might be located beside the gas chromatograph or some distance away, where the data can be transmitted via a modem to a central computer.

Analysis files, *e.g.*, temperature programme, runs tables, integration parameters, calibration tables, analysis reports and BASIC programs, are stored on a cartridge tape unit, built into the gas chromatograph.

Before the chromatographic analysis, both sample loops are purged with the gas sample. The analysis is controlled by a run table according to Fig. 2. A schematic diagram of the analysis sequence is shown in Fig. 3. The chromatographic conditions are listed in Table I and a chromatogram obtained from a typical natural gas sample is shown in Fig. 4.

At the beginning of the analysis, a sample from valve 1 is introduced on to the Porapak column, which separates oxygen, nitrogen and methane from carbon dioxide and ethane. The light components are further separated by a molecular sieve 13X column, which is connected in series to the Porapak column. After elution of methane, the molecular sieve column is isolated, and carbon dioxide and ethane are eluted from the Porapak column. Up to this point, the monitoring is carried out by the thermal conductivity detector. Now, the detector signal is switched to the flame-ionization detector and the Porapak column is back-flushed.

After 3.7 min, valve 3 is switched, and the sample is introduced into the capillary column. After 12 min, the column oven is programmed to 170°C at rate of 10°C/min.

* The program is available from Hewlett-Packard as a Software Note.

RUN TABLE:

```

0.00 ATTN 2↑8
0.01 VALVE 1 ON
2.50 CHART SPEED 0.7
2.60 VALVE 2 ON
3.70 VALVE 3 ON
6.20 EXTEND RT ON
7.00 SIGNAL B
7.01 ZERO
7.05 PEAK WIDTH 0.02
7.05 CHART SPEED 2
7.10 THRESHOLD -4
7.25 ATTN 2↑7
7.70 ATTN 2↑4
8.30 CHART SPEED 1.2
8.80 ATTN 2↑8
26.00 STOP

```

Fig. 2. Run table.

RESULTS AND DISCUSSION

The GC system was calibrated with a calibration sample, analysed under the same conditions as the sample gas. Quantitative results were obtained by normalizing the calibrated peaks to 100 %. Methane and ethane, eluted from the capillary column, were not used for quantitation. However, the total amounts obtained for methane and ethane can be used to correlate the data obtained from both the capillary and packed column systems. This correlation would be necessary if the sample amounts in both

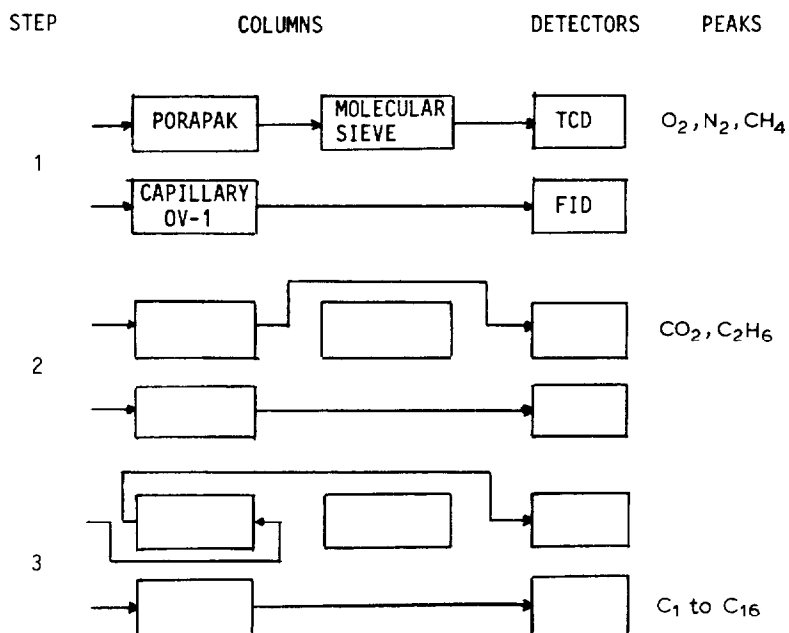


Fig. 3. Analysis sequence.

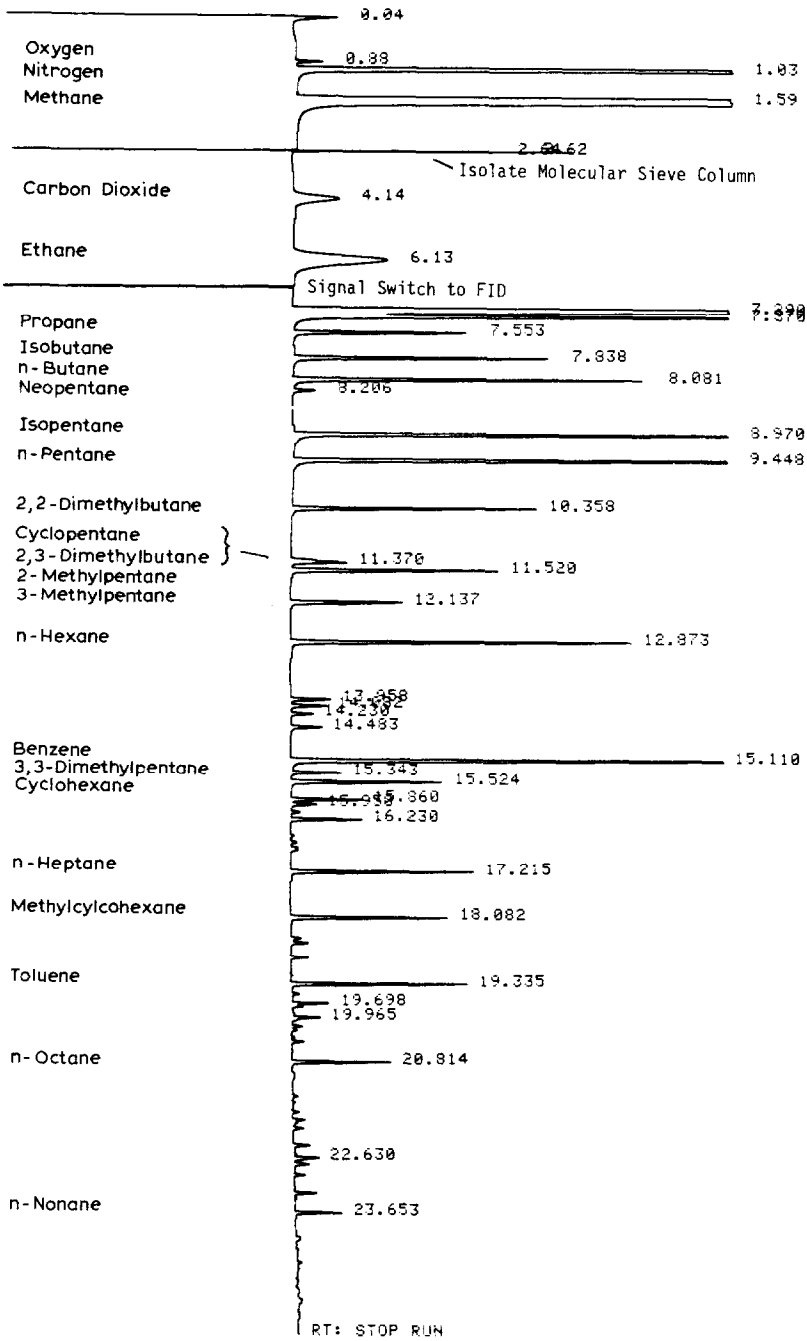


Fig. 4. Chromatogram of a natural gas sample. For conditions, see Table I.

TABLE I
CHROMATOGRAPHIC CONDITIONS

Instrument	Hewlett-Packard 5880A gas chromatograph
Columns	(1)Stainless steel, 6 ft. Porapak T × 4 ft. Porapak Q, 80–100 mesh (2)Stainless steel, 3 ft. molecular sieve 13X, 80–100 mesh (3)Fused silica, 50 m × 0.2 mm I.D., 0.5- μ m OV-1, P/N 19091S Opt. 001.
Carrier gas	Helium
Oven temperature profile	Initial value 35°C Initial time 12 min Programme rate 10°C/min Final value 170°C Final time 5 min

sample loops or the detector responses were to change from one analysis to another. Statistical data from eight consecutive analyses are given in Table II. These were been obtained without correlating the amounts of methane and ethane.

The oven temperature is limited to 190°C by the Porapak T column. At this temperature, hydrocarbons up to C₁₆ are easily eluted from the capillary column. The molecular sieve column is required only if oxygen is to be analysed. Oxygen is normally not present in natural gas, but it is often useful to have information on oxygen content as a means of detecting leaks in pipelines.

There is a time delay of 3.7 min between sample introduction into the two column systems. However, if simultaneous introduction were desired, a second integrator

TABLE II
STATISTICAL DATA, CALCULATED BY THE 5880 BASIC PROGRAM

Amounts in % (v/v).

Compound	Average	No. of Chromatograms	Standard deviation	
			Absolute	Relative (%)
Oxygen	0.103	8	0.002	1.609
Nitrogen	11.888	8	0.005	0.044
Methane	82.770	8	0.020	0.024
Carbon/Dioxide	0.948	8	0.003	0.340
Ethane	3.351	8	0.010	0.305
Propane	0.610	8	0.003	0.561
Isobutane	0.085	8	0.001	0.680
<i>n</i> -Butane	0.130	8	0.001	0.668
Neopentane	0.007	8	0.000	0.844
Isopentane	0.027	8	0.000	0.753
<i>n</i> -Pentane	0.026	8	0.000	0.910
2,2-Dimethylbutane	0.006	8	0.000	1.075
3-Methyl-Pentane	0.003	8	0.000	1.644
<i>n</i> -Hexane	0.009	8	0.000	1.074
Benzene	0.021	8	0.000	1.208
<i>n</i> -Heptane	0.004	8	0.000	1.204
Methyl-cyclo-hexane	0.004	8	0.000	1.599
Toluene	0.005	8	0.000	1.682
<i>n</i> -Octane	0.002	8	0.000	1.503
<i>n</i> -Nonane	0.001	8	0.000	2.546

channel would be necessary. The amount of sample introduced on to both channels can be optimized independently. For the packed column-thermal conductivity detector channel, a sample volume of 0.1 ml at atmospheric pressure was found to be suitable. The small amount of sample ensures 100 % detector linearity, even for highly concentrated components, such as methane. The amount of sample introduced into the capillary column can be adjusted by the size of the gas sample loop and also by the capillary splitting ratio. For the analysis shown in Fig. 4, a sample loop size of 1.0 ml and a split flow of 100 ml/min were used. Under these conditions, the minimum detectable level is around 1 ppm. If a lower detection limit is required, the split flow can be reduced to about 20 ml/min. However, under these conditions, the capillary column may be overloaded for propane. This means that the optimum amount of sample for the capillary column depends on the concentration range likely to be encountered in the sample.

ACKNOWLEDGEMENTS

Appreciation is expressed to Ruhrgas, F.R.G., for providing the natural gas sample and Dr. P. Larson, Hewlett-Packard, Avondale, PA, U.S.A., for providing the cross-linked column.

REFERENCES

- 1 *Annual Book of ASTM Standards, Standard D 1945-64, Analysis of natural gas by gas chromatography*, American Society for Testing and Materials, Philadelphia, PA, 1964.
- 2 *Natural Gas Analyzer, Hewlett-Packard Data Sheet, Publication No. 43-5953-1529*, Hewlett-Packard, Avondale, PA, 1980.
- 3 L. Huber and W.J.J. Leunissen, *Cost Savings Through Accurate Natural Gas Analysis, Hewlett-Packard Brochure* Hewlett-Packard, Waldbronn, 1983.
- 4 *ISO Standard 6569-1981, Natural Gas-Rapid Analysis by Gas Chromatography*, International Organization for Standardization, Geneva, 1981.
- 5 *ISO Standard 6568-1981, Natural Gas-Simple analysis by Gas Chromatography*, International Organization for Standardization, Geneva, 1981.
- 6 *ISO/DP 6974, Analysis of Hydrocarbons up to C₈ and Inert Gases by Gas Chromatography*, International Organization for Standardization, Geneva, 1982.
- 7 G. J. Van Rossum and B. J. Wolkotte, *GWF, Gas-Wasserfach: Gas/Erdgas*, 121 (1980) 47-54.
- 8 J.S. Stufkens and H.J. Bogaard, *Anal. Chem.*, 47 (1975) 383-386.