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ANALYSIS OF NATURAL GAS BY GAS CHROMATOGRAPHY

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SUMMARY

A method for the analysis of natural gas that is suitable for use in routine control analyses has been developed. A thermal conductivity detector is used for the determination of $N_2 + O_2$, CO_2 and C_1-C_2 hydrocarbons and a flame-ionization detector for other components, with programming of the column temperature. By concentrating C_6 and higher hydrocarbons in a short column section that can be disconnected during the analysis, a rapid and accurate analysis can be carried out by back-flushing. The integrator can be used to calculate real density and real calorific values simultaneously.

INTRODUCTION

To measure an amount of natural gas, especially in industrial situations, it is necessary to determine correctly all of the components that are used to express significant qualitative criteria, *i.e.*, true calorific values and true density.

Isothermal gas chromatography with a single column makes it possible to obtain only partial information on the total composition, this being dependent on the temperature and column length. Substantial improvements can be achieved by using temperature programming and detection with a thermal conductivity (TCD) and flame-ionization detector (FID) simultaneously¹. Even in this instance a portion of heavier components remains adsorbed on the column packing. The problem of the total analysis of natural gas is dealt with in ASTM Standard D 1945, which prescribes the determination of nitrogen, carbon dioxide and C_1-C_5 hydrocarbons as individual peaks, and C_6 and higher hydrocarbons as a sum from back-flushing. As an example, ASTM D 1945 describes three methods by Purcell and Gilson². Two of the methods concern isothermal analysis with back-flushing while the third uses temperature programming and back-flushing. All of the methods use a TCD. HP 5830 has been used to analyse natural gas³, in a system of three columns packed with Porapak Q,

30% DC 200 on Chromosorb W and molecular sieve 5A, with thermal conductivity detection. The procedure is fully automatic.

In this paper, an automatic method for the analysis of natural gas is described that is suitable for use in routine control analysis.

EXPERIMENTAL AND RESULTS

Apparatus

A Packard Model 419 gas chromatograph, equipped with a temperature-programmed column, TCD, dual FID, three eight-way-, two-position "Kuhnke" valves controlled either manually or pneumatically, W + W 10-mV recorder and a Spectra-Physics Autolab System I integrator for integration of the peak areas were used. The procedure consists in the separation of natural gas components on a column packed with Porapak R. The column is divided into two sections, which can be connected according to scheme I, II or III (Fig. 1). The first short section serves to concentrate the C_6 and higher hydrocarbon fractions, so that these fractions can be determined by back-flushing. The detection of oxygen + nitrogen, carbon dioxide and C_1 - C_2 hydrocarbons is performed with the TCD, while the other hydrocarbons are detected with the FID, the two detectors being arranged in a series.

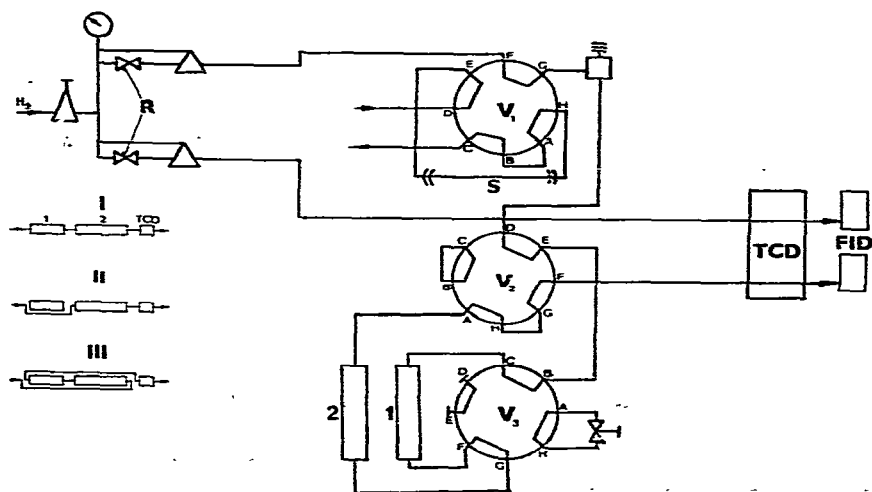


Fig. 1: Flow diagram of apparatus. R = Flow controllers; V_1 = sample valve; S = sample loop; V_2 = back-flush valve; V_3 = switch valve; 1 = column packed with Porapak R (1 m \times 2 mm I.D.); 2 = column packed with Porapak R (3 m \times 2 mm I.D.). I-III, connection schemes.

Chromatographic separation conditions

The dimensions of the analysis section of the column were: 1 m + 3 m \times 2 mm I.D. and those of the reference section were 4 m \times 2 mm I.D. The packing was Porapak R (80-100 mesh). The carrier gas (hydrogen) flow-rate was 20 ml in the analysis and reference sections; with an added gas (nitrogen) flow-rate of 15 ml/min and an air flow-rate of 300 ml/min. The TCD temperature was 150° with a detector current of 200 mA and the FID temperature was also 150°. The column temperature

was maintained isothermally at 30° for 1 min, then programmed from 30 to 180° at 15°/min, the final temperature being maintained for 9 min, followed by a cooling period of 10 min. The gas sample size was 0.25 ml and the recorder was operated at 10 mV.

Procedure

A sample of gas is introduced into the chromatograph through the eight-way valve V_1 (Fig. 1), equipped with a sample loop S of volume 0.25 ml. The Autolab System I is set to the "Run" mode and the pre-adjusted temperature programme is

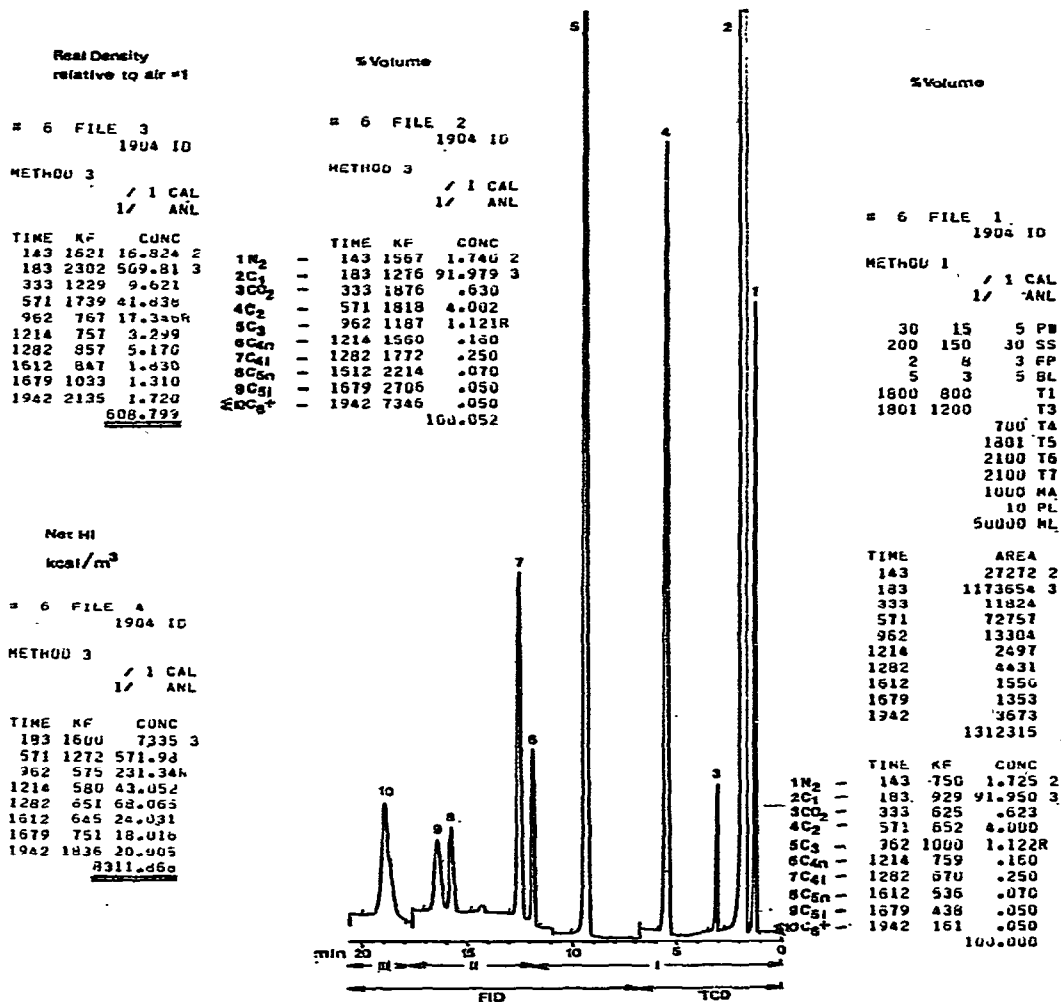


Fig. 2. Chromatogram of a natural gas sample. Peaks: 1 = air; 2 = methane; 3 = carbon dioxide; 4 = ethane; 5 = propane; 6 = isobutane; 7 = *n*-butane; 8 = isopentane; 9 = *n*-pentane; 10 = hexanes and heavier. In File 1 the gas composition is calculated by Method 1 (internal normalization). In File 2 the gas composition is calculated by Method 3 (external standard). In File 3, the real density is calculated by Method 3; the result is read by equating the scale factor 10^{-3} to 0.609. In File 4, the net calorific value (Net HI) is calculated by Method 3 to be 8311.9 kcal/m³.

set simultaneously. The two column sections are connected in series at the start and the integrator accepts the signal from the TCD. After the elution of ethane (7 min) the integrator is switched to the FID signal. As soon as *n*-pentane has been eluted from the short column section (12 min), this section is disconnected via the valve V_3 so as to store C_6 and higher hydrocarbon fractions; this procedure makes it possible to eliminate the need to resolve C_6 and higher hydrocarbon fractions and to speed up the analysis. When the elution of *n*-pentane from the second column section is completed (18 min), the two column sections are connected again (V_3) and back-flushed (V_2). The integration is performed after the analysis is completed and the columns are cooled simultaneously. The results are shown in Fig. 2.

Quantitative determinations were performed with a standard mixture purchased from Messer-Griesheim (Duisburg, G.F.R.). The calculation of concentrations from peak areas is possible either by internal normalization or the external standard method (Methods 1 and 3, in Autolab System I language).

The calibration consists in correlating the concentrations of the components of a standard mixture with the relating peak areas that are marked by their retention times, the integrator being set in the "Calibration" mode. The Autolab System I uses these data to calculate the corresponding KF (calibration values), depending on the method selected. These KF values are used to calculate results for the sample being analysed, the "Analysis" mode being used. To calculate the results, Method 1 was chosen, the advantages of which are that the results are corrected to the contents of all components and they are independent of the exact amount injected. The advantage of Method 3, in which the concentrations are calculated by comparing the peak areas of the sample and the standards, can be used in the analysis of components of low concentration.

Method 3 can be used to calculate the characteristic constants real density (RD) or real calorific value (RCV). In this instance it is possible to add the real densities and real calorific values of the pure components to the corresponding peak areas and to calculate new KF values that can be used to calculate RD and RCV of samples. The Autolab System I makes it possible to store different calculation data in four independent memory files. The results obtained by Method 1 can be compared with the results obtained by Method 3 (Fig. 2). Method 1 was stored in File 1, Method 3 in File 2, the data to calculate RD in File 3 and those to calculate RCV in File 4.

DISCUSSION

The combination of a Packard Model 419 gas chromatograph with an Autolab System I integrator proved to be especially useful, and the method has the following advantages:

- (1) It complies with ASTM Standard D 1945.
- (2) The automatic switching over of the integrator from the TCD to the FID permits the accurate determination of all components.
- (3) The storage of the higher hydrocarbons in the short column section concentrates them to a single sharp peak, which makes the integration easier and more exact.
- (4) The pressure pulses due to switching over the valves, observable with the

TCD, and the irregularity of the baseline with temperature programming, are eliminated by using the FID.

(5) By using the Autolab System I it is possible to calculate the exact composition of natural gas and the real density and real calorific values simultaneously during the analysis, and thus to eliminate the need for expensive equipment for their determination.

REFERENCES

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- 2 J. E. Purcell and C. P. Gilson, *Chromatogr. Newsl.*, 1, No. 2 (1972) 45.
- 3 L. E. Green, *Hewlett Packard Technical Paper*, No. 57 (1974).