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QUANTITATIVE ANALYSIS OF NATURAL GAS IN A SINGLE RUN BY THE USE OF PACKED AND CAPILLARY COLUMNS

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SUMMARY

The chromatographic separation of oxygen, nitrogen, carbon dioxide and approximately 60 hydrocarbons from C_1 to C_{10} was achieved by utilizing a combination of packed and capillary columns. Fifty components were identified from a retention time table. The sample was injected via two time-programmed loops into packed and capillary columns with thermal conductivity and flame-ionization detection. Columns were molecular sieve 13X, Porapak R and Chrompack Sil 5 (fused silica). The hydrocarbons were analysed by split injection and temperature programming, starting at −30°C, and the permanent gases were analysed isothermally at 50°C in a special compartment outside the main oven.

Quantification was achieved by the use of relative weight response factors, eliminating the need for repeatable sample size and frequent recalibrations. The precision was in the range 0.2–1.4% (R.S.D.) for major components and about 6% for minor components. Long-term consistency in the analytical data from the routine analysis of hydrocarbon reservoir fluids indicates good accuracy.

INTRODUCTION

Natural gas analysis is an important part of the analysis required to describe the reservoir fluid in oil and gas fields. Detailed information on the composition provides data for a better description of the behaviour of reservoir fluid during production. It will also ensure a better quantitative evaluation of reservoirs and give a better estimate of the potential value of fields.

The low-pressure gas samples involved in such studies are often saturated with heavy components having carbon numbers up to 10. In gas condensate systems such components may have a significant influence on the physical properties of the reservoir fluid. It is therefore of great importance to quantify and identify these components in order to give correct data input to the evaluation of reservoir fluids.

Our laboratories have over the last few years developed a routine natural gas analysis. It consist of a high-resolution capillary separation of the hydrocarbons and a system of packed columns for the separation of the inorganic gas components such as carbon dioxide, nitrogen and oxygen. Earlier reports suggested the use of a combination of packed and thick-film capillary columns to separate hydrocarbons in natural gas[1]. Our experience is that better analytical results are achieved by analysing all hydrocarbons on one thin-film capillary column at sub-ambient temperature.

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TABLE I

ANALYTICAL CONDITIONS FOR ORGANIC ANALYSIS

Parameter	*Conditions*	*Parameter*	*Conditions*
Oven temperature programme	Initial value: −30°C, 6 min. Rate: 6°C/min Final value: 160°C Cryogenic medium: liquid CO_2	Detector	Type: Flame ionization Fuel gas: H_2, 30 ml/min Make-up gas: N_2, 30 ml/min Temperature: 200°C
Analytical column	Type: Wall-coated open tubular (WCOT) capillary, fused silica Liquid phase: CP Sil 5, Chrompack Carrier gas: He, linear velocity, 21 cm/min Length: 50 m Inside diameter: 0.22 mm Film thickness: 0.40 μm	Sampling	Type: Sample loop valve Sample size: 1 ml at 1 atm Split injector type: Packed Jennings tube Split ratio: 1:100 Valve temperature: 150°C Injector temperature: 150°C

TABLE II

ANALYTICAL CONDITIONS FOR INORGANIC ANALYSIS

Parameter	*Conditions*	*Parameter*	*Conditions*
Temperature cycle, packed columns	Initial value: 50°C, 5 min Second value: 180°C, 15 min Final value: 50°C	Detector	Type: Thermal conductivity, single element Reference flow: He, 25 ml/min Modulator flow: He, 50 ml/min Temperature: 200°C
Analytical columns	Column 1: Porapak R, 80–100 mesh Length: 3 m Outside diameter: 1/8 in Column 2: Molecular sieve 13X, 80–100 mesh Length: 1 m Outside diameter: 1/8 in. Carrier gas: He, 25 ml/min	Sampling	Type: Sample loop valve Sample size: 0.1 ml at 1 atm Valve temperature: 150°C

EXPERIMENTAL

Apparatus

The gas chromatograph employed was a Hewlett-Packard 5880 A, equipped with a level IV integrator. The instrument conditions are given in Tables I and II. The capillary column is placed in the main oven. The packed columns are placed outside the chromatograph oven in an insulated compartment, which is kept isothermal by an auxiliary temperature control from the 5880 A. A small fan circulates the air inside the compartment. After the analysis, the packed columns are reconditioned by a temperature cycle, and ready for a new sample when the capillary run is finished. The gas sample is introduced into the columns by two time-programmed sample loops. Valve, column and signal switching are marked on the chromatogram shown in Fig. 1.

Calculation and calibration

The quantitative calculation of the separate components is based on the assumption of full recovery of the sample. The area distribution of hydrocarbons is measured from the capillary chromatogram. Each area is then multiplied by the relative response factor for that particular component to convert to weight distribution.

From the thermal conductivity chromatogram, the weights of nitrogen and carbon dioxide relative to methane are determined. In other words methane acts as an internal standard to quantify nitrogen and carbon dioxide. In our analysis oxygen originates from air contamination and is removed together with some of the nitrogen area in the same proportion as in air. Finally, the sum of components is normalized to 100% by weight. The calculation can be expressed by

$$\left[\sum_{i=CH_4}^{C_{10}} A_i R_i + (A_{N_2} R_{N_2} + A_{CO_2} R_{CO_2}) \frac{A_{CH_4(FID)} R_{CH_4}}{A_{CH_4(TCD)}} \right] K = 100$$

where

A_i	=	flame-ionization detection (FID) area of a component i;
A_{N_2}	=	thermal conductivity detection (TCD) area of N_2;
A_{CO_2}	=	TCD area of CO_2;
$A_{CH_4(TCD)}$	=	TCD area of CH_4;
$A_{CH_4(FID)}$	=	FID area of CH_4;
R_i	=	FID weight response, component i relative n-C_7;
R_{CH_4}	=	FID weight response, CH_4 relative n-C_7;
R_{N_2}	=	TCD weight response, N_2 relative CH_4;
R_{CO_2}	=	TCD weight response, CO_2 relative CH_4;
K	=	normalization constant.

When this procedure is used, the quantification is independent of repeatable sample size, provided that the amounts of individual components are within the linear dynamic range of the detector.

Calibration is now a matter of determining the relative response factors, R_i,

R_{N_2} and R_{CO_2}. A primary standard gas mixture (Matheson Gas Products, Oevel, Belgium) with components of nitrogen, carbon dioxide and hydrocarbons from C_1 to n-C_5 was used for the light components. A liquid blend of paraffinic, naphthenic and aromatic hydrocarbons from n-C_5 to n-C_{10} was used for the heavier components. Gas and liquid were analysed separately, and the multiplication factor R_i for converting from area% to weight% was determined experimentally. The factor for n-C_7 is defined as 1 by choice, and the two sets of factors are unified by a common factor for n-C_5.

From the TCD analysis, the constant R_{CO_2} is determined from

$$R_{CO_2} = \frac{\text{Weight\% } CH_4 \cdot A_{CO_2}}{\text{Weight\% } CO_2 \cdot A_{CH_4}}$$

and similarly for nitrogen.

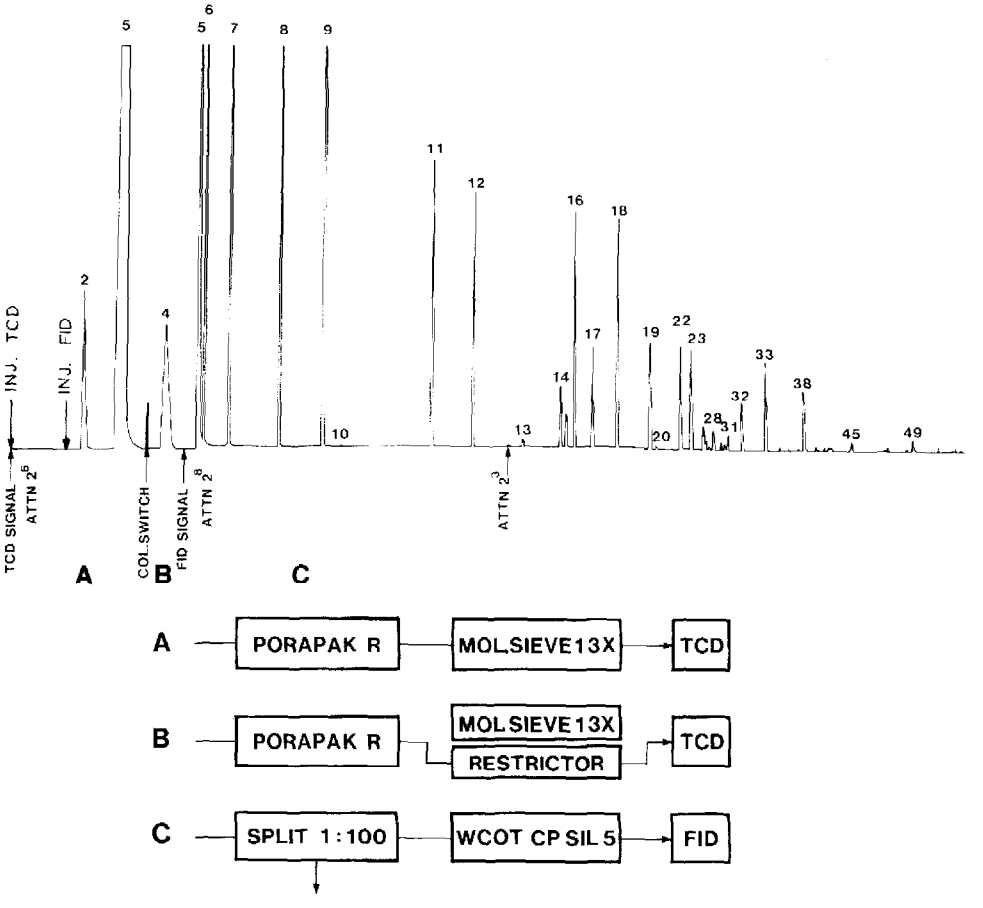

Fig. 1. Typical chromatogram and column configuration. Peak numbers correspond to calibration numbers given in Table III.

TABLE III

COMPOSITION OF A NATURAL GAS SAMPLE, AVERAGE OF 8 ANALYSES

Calibration No.	*Component*	*Weight%*	*R.S.D. (%)*	*Calibration No.*	*Component*	*Weight%*	*R.S.D. (%)*
2	Nitrogen	1.6542	0.5	26	2,3-Dimethylpentane	0.0045	5.6
4	Carbon dioxide	2.3040	0.6	27	1,1-Dimethylcyclopentane	0.0025	5.6
				28	3-Methylhexane	0.0125	5.1
5	Methane	60.5818	0.2	29	1,*cis*-3-Dimethylcyclopentane	0.0060	5.5
6	Ethane	15.5326	0.2	30	1,*trans*-3-Dimethylcyclopentane	0.0060	5.5
7	Propane	12.3819	0.2	31	1,*trans*-2-Dimethylcyclopentane	0.0094	5.0
8	Isobutane	2.0616	0.9	32	*n*-Heptane	0.0290	3.8
9	*n*-Butane	3.2129	1.4				
10	2,2-Dimethylpropane	0.0074	2.0	33	Methylcyclohexane	0.0565	3.4
11	Isopentane	0.7677	3.2	35	Ethylcyclopentane	0.0035	3.8
12	*n*-Pentane	0.6601	3.9	36	1,*trans*-2,*cis*-4-Trimethylcyclopentane	0.0004	185.2
				37	1,*trans*-2,*cis*-3-Trimethylcyclopentane	0.0002	282.8
13	2,2-Dimethylbutane	0.0059	5.4	38	Toluene	0.0436	5.6
14	Cyclopentane	0.0395	6.0	39	2-Methylheptane	0.0039	6.6
15	2,3-Dimethylbutane	0.0212	6.0	40	3-Methylheptane	0.0025	8.0
16	2-Methylpentane	0.1404	6.0	41	1,*cis*-3-Dimethylcyclohexane	0.0044	7.6
17	3-Methylpentane	0.0603	6.3	42	1,*trans*-4-Dimethylcyclohexane	0.0022	7.4
18	*n*-Hexane	0.1302	6.5	45	Normaloctane	0.0099	10.0
				47	*m* + *p*-Xylene	0.0029	15.7
19	Methylcyclopentane	0.0684	6.8	48	*o*-Xylene	0.0029	13.2
20	2,4-Dimethylpentane	0.0032	6.8	49	*n*-Nonane	0.0137	12.9
21	2,2-Dimethylpentane	0.0001	138.1				
22	Benzene	0.0648	6.5		Unidentified decanes	0.0081	22.4
23	3,3-Dimethylpentane	0.0005	9.5				
24	Cyclohexane	0.0624	6.2				
25	2-Methylhexane	0.0145	5.5				

The calibration is based on an average of a minimum of six determinations, which at the same time gives an indication of the precision. However, precision is always better on standard mixtures than on real gas samples, owing to fewer components and higher concentrations.

The calibration is probably dependent on the detector design, injection system, etc., but once it is obtained it will be valid as long as no major changes are made in instrumental set-up. Only infrequent tests are required to check that the calibration stays within limits at a given confidence level[2].

RESULTS AND DISCUSSION

A typical chromatogram of a lean natural gas sample is shown in Fig. 1; 43 peaks were identified from a retention time table, obtained from a high-resolution gas chromatographic–mass spectrometric study, combined with a comparison of retention times of pure components. In Table III the calibration number from the retention time table is given in the first column, followed by the name of the most abundant molecule in the peak. An average $\bar{X}$ of 8 analyses was used to calculate the weight-%, and the relative standard deviation (R.S.D.) = (S.D./$\bar{x}$) × 100% is given. The precision decreases from 0.2 to 4% from methane to pentane, but stays at approximately 6% for heavier compounds. Very small peaks are detected at random, causing a dramatic increase in the R.S.D.

The lean gas sample contains only about 1% of components heavier than *n*-pentane, compared with 5–10% for a rich sample. As the amount of a component influences the precision, a richer sample may give different figures for relative standard deviation[3].

Accuracy is very dependent on the calibration, but if a primary gas standard is used, this error should not dominate at the precision level given in Table III. Experience over the years with samples taken at different places and times from the same oil reservoir indicates satisfactory accuracy for the method, including the sampling error.

CONCLUSION

A system for the routine analysis of natural gas, based on packed and capillary columns and sub-ambient temperature programming, has been developed. The method is independent of repeatable sample size. The calibration stays valid for years and the precision and accuracy are satisfactory over the full range of components in natural gas. Because the resolution is high, all significant components can be identified and quantified from 100% down to 10 ppm. The same instrument may be used for natural gas and oil and liquid condensates without changing the column.

Investigations on the effect of possible unlinear detector response will be carried out in the nearest future.

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