Development and Validation of a Chromatographic Method for the Determination of C1-C8 Hydrocarbons, O_2, N_2 and CO_2 in Natural Gas

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A gas chromatographic method was developed and validated for determination of hydrocarbons (C1-C8), oxygen, nitrogen and carbon dioxide in natural gas samples. The experiments were carried out on a Varian CP3800 gas chromatograph (GC). The method showed good linearity, accuracy and precision. Advantages of this validated method consist in parallel determination of C1-C8 hydrocarbons and permanent gases in natural gas, short analysis time and good sensitivity for all analytes.

Keywords: validation, chromatographic method, natural gas, hydrocarbons

The natural gas is one of the vital components of the world's supply of energy, satisfying the actual demand of population. Although this is considered as a *clean* fuel compared to other fossil fuels, and it is also a source of hydrocarbons for petrochemical feed stocks. Many researchers turned their attention to natural gas field, due to its high composition of methane, being an important contributor for the production of other products such as hydrogen, syngas and also helium [1-6].

Beside methane and various amounts of hydrocarbons, natural gas can also contain other contaminants, such as water vapours, nitrogen, oxygen, carbon dioxide, helium, possibly hydrogen sulphide and ammonia [7-10]. Raw production natural gas must be purified before being distributed by companies. Thus, by removing the impurities the calorific value of natural gas increases and the pipelines and equipment corrosion is avoided [11-13].

Typical composition of natural gas is given in table 1 [14]. The exact composition at any site will vary among the different regions.

Identification and quantification of hydrocarbons and impurities represent an important criterion, having a significant impact on the price of natural gas. In this respect, different methods can be employed with more or less accuracy. The most common and simple instruments are portable analysers, more suitable for industrial usage. These techniques have a disadvantage, namely, the hydrocarbons, except methane, are quantified as a total and not separately. Regarding this, various chromatographic methods have been described for the determination of source and natural gas quality [15-17]. Literature mentions a GC method with a single column and with a pulsed discharge helium ionization detector (PDHID), used for the analysis of C1-C5 hydrocarbons, but this was not precise compared with multi-column methods [18-20].

Table 1
TYPICAL COMPOSITION OF NATURAL GAS

Component	Range (%Vol)
Methane	87.0-96.0
Ethane	1.8-5.1
Propane	0.1-1.5
Isobutane	0.01-0.3
normal-Butane	0.01-0.3
Isopentane	Trace to 0.14
normal-Pentane	Trace to 0.14
Hexane	Trace to 0.06
Nitrogen	1.3-5.6
Carbon Dioxide	0.1-1.0
Oxygen	0.01-0.1
Hydrogen	Trace to 0.02

The aim of this study is to elaborate and validate a chromatographic method for the simultaneous determination of C1-C8 hydrocarbons, oxygen, nitrogen and carbon dioxide in natural gas.

The method validation is necessary in the practice of chromatographic analysis for demonstrating the efficiency of a properly implemented quality management system [21, 22]. Consequently, the method linearity, selectivity, repeatability, accuracy, limit of detection (LOD) and limit of quantification (LOQ) were evaluated with the aid of a Varian CP3800 gas chromatographic system equipped with specific analytical columns, ionization and thermal conductivity detection.

Experimental part

The method can be applied to the simultaneous determination of C1-C8 hydrocarbons, oxygen, nitrogen and carbon dioxide in natural gas, in the measurement range of the typical composition of natural gas (table 1).

Gas chromatography system

The Varian CP3800 gas chromatography system (Varian Instrumentation, USA) consists of a sample admission valve, two split injection valves, a switching valve, CP-Al_2O_3/KCl analytical separation column (25 m x 0.32 mm internal diameter), CP-PoraBOND Q-HT analytical separation column (27.5 m x 0.32 mm internal diameter), CP-Molsieve 5Å analytical separation column (50 m x 0.53 mm internal diameter), a thermostat oven, a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Stainless steel tubing is used throughout the sampling system and connections were tested for integrity by pressurizing the system with Helium and verifying for leaks with an electronic gas detector (Edwards - Gas Check B4, United Kingdom).

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Table 2
GAS STANDARDS USED FOR GC CALIBRATION

Analyte	Standard (%Vol)						
	1	2	3	4	5	6	7
Methane	balance (86.5)	balance (81.4)	balance (98.76)	balance (97)	balance (91.77)	balance (95.815)	balance (64.06)
Ethane	1	5	0.5	0.05	0.005	0.01	10.45
Propane	2	4	0.1	0.05	0.01	0.499	0.99
Isobutane	1	2	0.05	0.01	0.005	0.101	0.5
n-Butane	1	2	0.05	0.01	0.005	0.101	0.5
Neo-Pentane	0.5	1	0.01	0.35	0.005	0.201	0.1
Isopentane	0.5	1	0.01	0.35	0.005	0.05	0.1
n-Pentane	0.5	1	0.01	0.35	0.005	0.05	0.1
2.2Dimethylbutane	-	-	-	0.1	0.02	0.005	0.3
2.3Dimethylbutane	-	-	-	0.1	0.02	0.005	0.3
3Methylpentane	-	-	-	0.1	0.02	0.006	0.3
2Methylpentane	-	-	-	0.1	0.02	0.005	0.3
nHexane	-	-	-	0.1	0.01	0.001	0.25
2.4Dimethylpentane	-	-	-	0.1	0.01	0.002	0.25
2.2.3Trimethylbutane	-	-	-	0.15	0.01	0.002	0.2
2Methylhexane	-	-	-	0.1	0.015	0.002	0.2
3Methylhexane	-	-	-	0.15	0.01	0.002	0.2
3ethylpentane	-	-	-	0.15	0.01	0.001	0.2
n-Heptane	-	-	-	0.03	0.01	0.001	0.2
Isooctane	-	-	-	0.02	0.009	0.001	0.1
n-Octane	-	-	-	0.02	0.01	0.001	0.1
Methylcyclohexane	-	-	-	0.02	0.01	0.001	0.1
Cyclohexane	-	-	-	0.02	0.01	0.001	0.1
Benzene	-	-	-	0.01	0.006	0.001	0.05
Toluene	-	-	-	0.01	0.005	0.001	0.05
Carbon Dioxide	1	2	0.3	0.1	0.01	0.505	5
Oxygen	1	0.1	0.02	0.4	0.08	0.05	5
Nitrogen	5	0.5	0.2	0.05	7.89	1.51	10

The Varian CP3800 is equipped with STAR GC Workstation software, version 6.3 (Varian Instrumentation, USA), for operation and data interpretation.

GC analysis /Measurement procedure

The temperature and pressure programming was necessary in order to elute the more strongly retained components from the CP-Al_2O_3/KCl column. The temperature was held at 40°C and the pressure at 39 psi for 4 min and then ramped at 200°C and 43 psi, respectively, and held so that a total run time of 32 min was obtained. The column flow was initially 20 mL min^{-1}. O_2 and N_2 elute from CP-PoraBOND Q-HT column and then pass to CP-Molsieve 5Å column, where they are separated.

Via a switching valve, the thermal conductivity detector assures the quantification of CO_2 and also of O_2 and N_2. Flame ionization detector provides the quantification of hydrocarbons. Methane can also be detected by TCD, but the signal is significantly smaller than FID detector.

The temperatures of FID and TCD were set at 250°C and 150°C, respectively. The temperature of the injection valves was set at 50°C, the injection volume was 500 µL and a split ratio of 1:5 was employed.

Materials and calibration standards

The carrier gas (Helium, purity: 99.999%Vol or better), the valve actuator gas (compressed air) and the FID combustion gas (Hydrogen, purity: 99.999%Vol or better) were purchased from Messer Romania Gaz.

To establish and to control the gas flow from cylinders through the gas chromatographic system, appropriate reducers purchased from Linde Gaz Romania were used.

The samples were obtained by ICIT Ramnicu Valcea from different regions of Romania.

Seven mixtures of hydrocarbons and permanent gases in methane, obtained from Air Liquide, Romania, were used for instrument calibration.

The balance gas concentrations (methane) were calculated as the difference (the total volume-100%Vol minus the others impurities) and they were confirmed in-house by a validated mass spectrometry method, using a VG Prolab Advanced (Thermo Electron Corporation, United Kingdom). The standard concentrations are presented in table 2.

Validation procedure

The validation procedure was performed according to the guidelines of the Eurachem Guide - The Fitness for Purpose of Analytical Methods, based on the criteria: selectivity, linearity, repeatability, accuracy, limit of detection (LOD), limit of quantification (LOQ) and evaluation of uncertainty [21].

Results and discussions

C1-C8 hydrocarbons, carbon dioxide, oxygen and nitrogen were separated, figure 1 presenting a typical chromatogram recorded for a natural gas sample.

Selectivity of the method

Selectivity was evaluated by examining the relative standard deviation (%RSD) of the retention times recorded in a 5 injections set. The retention times for all components, the average retention times and relative standard deviations are collected in table 3. The method is declared selective, because in all cases the relative standard deviation is less than 0.5 %.

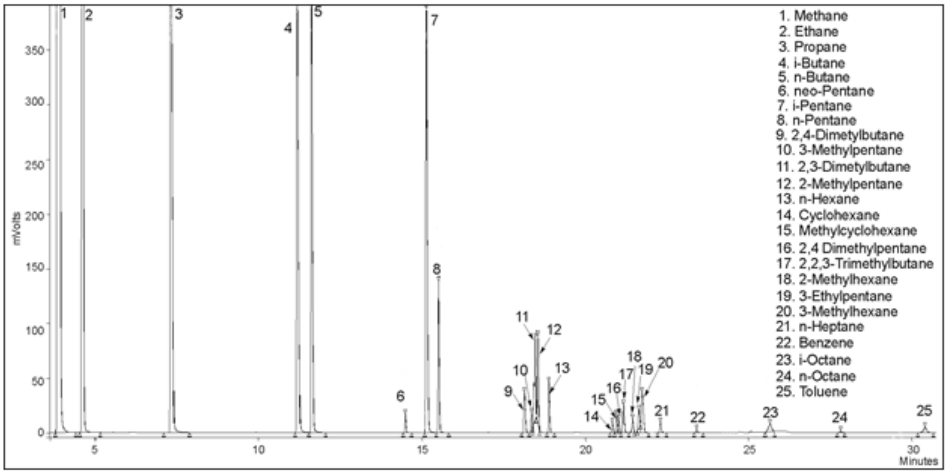

Fig.1 Typical chromatogram of C1-C8 hydrocarbons on the FID

Linearity

Experiments run at seven concentration levels for main components and four concentration levels for secondary components. Table 4 presents a good linearity, obtained for all components, with coefficients of determination higher than 0.995.

Limit of detection (LOD) and limit of quantification (LOQ)

The *limit of detection* is expressed as a concentration or quantity derived from the smallest signal that can be detected with reasonable certainty using an analytical procedure. The *limit of quantification* is the lowest concentration of analyte that can be quantitatively determined with an acceptable level of repeatability and accuracy, and it is always bigger than the limit of detection. The detection and quantification limits for hydrocarbons were obtained by replicate analysis of a sample (N_2, purity: 99.999%Vol) by multiplying the standard deviation by 3 and 10, respectively.

Due to different response and sensitivity of TCD compared to FID and to remove any suspicion regarding the contamination of sample with atmospheric air, the detection and quantification limits for permanent gases were performed by replicate analysis of a reference

Table 3

METHOD SELECTIVITY

Analyte	Retention time (min)					Average (min)	Standard deviation (min)	RSD (%)
	1	2	3	4	5			
Methane	3.958	3.959	3.960	3.958	3.957	3.958	0.00114	0.02880
Ethane	4.656	4.657	4.656	4.657	4.652	4.656	0.00207	0.04454
Propane	7.409	7.410	7.408	7.407	7.408	7.4084	0.00114	0.01539
Isobutane	11.257	11.257	11.258	11.259	11.260	11.258	0.00130	0.01158
n-Butane	11.691	11.690	11.688	11.691	11.690	11.690	0.00122	0.01048
Neo-Pentane	14.530	14.540	14.540	14.540	14.540	14.538	0.00447	0.03076
Isopentane	15.222	15.222	15.226	15.222	15.222	15.223	0.00179	0.01175
n-Pentane	15.577	15.570	15.580	15.577	15.579	15.577	0.00391	0.02511
2.2Dimethylbutane	18.170	18.169	18.169	18.170	18.169	18.169	0.00055	0.00301
3Methylpentane	18.415	18.415	18.419	18.418	18.410	18.415	0.00351	0.01904
2.3Dimethylbutane	18.480	18.490	18.470	18.480	18.500	18.484	0.01140	0.06168
2Methylpentane	18.624	18.625	18.625	18.627	18.625	18.625	0.00110	0.00588
n-Hexane	18.960	18.965	18.962	18.963	18.962	18.962	0.00182	0.00958
Cyclohexane	20.912	20.910	20.914	20.912	20.913	20.912	0.00148	0.00709
Methylcyclohexane	21.038	21.037	21.038	21.037	21.040	21.038	0.00122	0.00582
2.4Dimethylpentane	21.109	21.108	21.109	21.108	21.105	21.108	0.00164	0.00778
2.2.3Trimethylbutane	21.200	21.240	21.230	21.250	21.220	21.228	0.01924	0.09061
2Methylhexane	21.534	21.534	21.534	21.533	21.536	21.534	0.00110	0.00509
3ethylpentane	21.770	21.775	21.780	21.775	21.777	21.775	0.00365	0.01675
3Methylhexane	21.830	21.835	21.828	21.827	21.831	21.830	0.00311	0.01427
n-Heptane	22.387	22.387	22.388	22.389	22.387	22.388	0.00089	0.00400
Benzene	23.492	23.490	23.491	23.493	23.492	23.492	0.00114	0.00485
Isooctane	25.393	25.390	25.390	25.391	25.393	25.391	0.00152	0.00597
n-Octane	27.948	27.948	27.948	27.949	27.948	27.948	0.00045	0.00160
Toluene	30.550	30.549	30.549	30.560	30.570	30.556	0.00929	0.03040
Carbon Dioxide	2.748	2.745	2.749	2.744	2.749	2.747	0.00235	0.08537
Oxygen	6.555	6.561	6.554	6.530	6.501	6.540	0.02491	0.38093
Nitrogen	7.862	7.861	7.855	7.869	7.856	7.861	0.00559	0.07117

Accuracy

The accuracy of the procedure is measured as the difference between the measured value and the certified value (equation 1). Table 5 presents the certified values of components in standard, the average values of 7 replicate measurements for each standard and the values of accuracy.

$$Accuracy\% = \frac{\left|\overline{C}_{exp} - C_{th}\right|}{C_{th}} x100 \qquad (1)$$

Table 4

METHOD LINEARITY

Component	Number of Standards	Concentration range (%Vol)	Slope	Correlation coefficient, R^2
	7			
Methane	7	64.06-98.76	1.003116	0.999911
Ethane	7	0.005-10.45	1.001187	0.999996
Propane	7	0.01-4	0.999995	0.999989
Isobutane	7	0.005-2	0.989657	0.999988
n-Butane	7	0.005-2	1.002539	0.999861
Neo-Pentane	7	0.005-1	1.001709	0.999736
Isopentane	7	0.005-1	1.006759	0.999844
n-Pentane	7	0.005-1	0.996292	0.999764
2.2Dimethylbutane	4	0.005-0.3	1.033486	0.999816
2.3Dimethylbutane	4	0.005-0.3	0.998620	0.998557
3Methylpentane	4	0.006-0.3	0.965772	0.999885
2Methylpentane	4	0.005-0.3	0.997694	0.998639
n-Hexane	4	0.001-0..25	0.994068	0.998040
2.4Dimethylpentane	4	0.001-0.25	0.998424	0.999981
2.2.3Trimethylbutane	4	0.002-0.2	1.000539	0.999709
2Methylhexane	4	0.002-0.2	1.049619	0.995334
3Methylhexane	4	0.002-0.2	1.090696	0.996275
3ethylpentane	4	0.001-0.2	0.991102	0.999491
n-Heptane	4	0.001-0.2	0.979944	0.999890
Isooctane	4	0.001-0.1	0.992909	0.999891
n-Octane	4	0.001-0.1	1.004719	0.999566
Methylcyclohexane	4	0.001-0.1	0.962194	0.999852
Cyclohexane	4	0.001-0.1	0.992683	0.999212
Benzene	4	0.001-0.05	1.024856	0.999248
Toluene	4	0.001-0.05	0.978340	0.999887
Carbon Dioxide	7	0.01-5	0.995178	0.999976
Oxygen	7	0.02-5	0.982917	0.999960
Nitrogen	7	0.05-10	1.005123	0.999518

Table 5

METHOD ACCURACY

Analyte	Certified value %Vol	No. of replicates	Average %Vol	Accuracy %
Methane	64.06	7	64.04	0.031
Ethane	10.45	7	10.44	0.096
Propane	0.99	7	0.970	2.020
Isobutane	0.50	7	0.510	2.000
n-Butane	0.50	7	0.490	2.000
Neo-Pentane	0.10	7	0.098	2.000
Isopentane	0.10	7	0.098	2.000
n-Pentane	0.10	7	0.105	5.000
2.2Dimethylbutane	0.30	7	0.295	1.667
2.3Dimethylbutane	0.30	7	0.310	3.333
3Methylpentane	0.30	7	0.290	3.333
2Methylpentane	0.30	7	0.308	2.667
n-Hexane	0.25	7	0.245	2.000
2.4Dimethylpentane	0.25	7	0.254	1.600
2.2.3Trimethylbutane	0.20	7	0.195	2.500
2Methylhexane	0.20	7	0.210	5.000
3Methylhexane	0.20	7	0.230	15.000
3ethylpentane	0.20	7	0.220	10.000
n-Heptane	0.20	7	0.190	5.000
Isooctane	0.10	7	0.090	10.000
n-Octane	0.10	7	0.110	10.000
Methylcyclohexane	0.10	7	0.109	9.000
Cyclohexane	0.10	7	0.090	10.000
Benzene	0.05	7	0.047	6.000
Toluene	0.05	7	0.055	10.000
Carbon Dioxide	5.00	7	4.950	1.000
Oxygen	5.00	7	5.040	0.800
Nitrogen	10.00	7	10.080	0.800

Table 6
ANALYTE CONCENTRATIONS AFTER TEN RUNS

Analyte (ppmv)	Run									
	1	2	3	4	5	6	7	8	9	10
Methane	0.07	0.97	1.00	0.67	0.56	0.12	1.12	0.11	0.78	0.09
Ethane	0.17	0.09	0.49	0.37	0.06	0.12	0.11	1.11	0.78	1.09
Propane	0.13	0.22	0.82	0.66	0.16	0.02	0.92	0.01	0.08	0.79
Isobutane	0.09	0.07	0.23	0.67	0.18	0.14	1.02	0.01	0.109	0.26
n-Butane	0.009	0.16	0.08	0.05	0.623	0.67	0.18	0.08	0.79	0.05
Neo-Pentane	0.67	0.22	0.34	0.055	0.07	0.007	0.07	0.23	0.67	0.623
Isopentane	0.004	0.07	0.007	0.06	0.69	0.06	0.87	0.09	0.05	0.8
n-Pentane	0.87	0.09	0.05	0.07	0.23	0.67	0.79	0.18	0.055	0.6
2.2Dimethylbutane	0.37	0.05	0.623	0.055	0.49	0.37	0.06	0.12	0.09	0.7
2.3Dimethylbutane	0.028	0.07	0.80	0.06	0.69	0.37	0.09	0.67	0.07	0.67
3Methylpentane	0.09	0.009	0.6	0.18	0.055	0.36	0.06	0.69	0.51	0.92
2Methylpentane	0.37	0.09	0.7	0.66	0.16	0.02	0.92	0.01	0.67	1.02
n-Hexane	0.019	0.37	0.67	0.055	0.055	0.67	0.18	0.055	0.23	0.18
2.4Dimethylpentane	0.67	0.009	0.87	0.18	0.055	0.36	0.18	0.055	0.36	0.07
2.2.3Trimethylbutane	0.06	0.06	0.69	0.37	0.09	0.70	0.07	0.23	0.67	0.87
2Methylhexane	0.023	0.04	0.09	0.66	0.16	0.02	0.92	0.01	0.08	0.36
3Methylhexane	0.37	0.47	0.07	0.67	0.18	0.23	0.06	0.69	0.23	0.05
3ethylpentane	0.056	0.007	0.51	0.37	0.09	0.70	0.87	0.09	0.05	0.623
n-Heptane	0.061	0.07	0.67	0.18	0.055	0.36	0.06	0.69	0.37	0.8
Isooctane	0.18	0.055	0.36	0.37	0.09	0.70	0.87	0.09	0.05	0.6
n-Octane	0.37	0.903	0.9	0.66	0.16	0.02	0.92	0.01	0.08	0.7
Methylcyclohexane	0.07	0.337	0.57	0.67	0.18	0.055	0.06	0.69	0.23	0.67
Cyclohexane	0.011	0.005	0.05	0.11	0.123	0.02	0.12	0.001	0.08	0.19
Benzene	0.07	0.004	0.05	0.07	0.006	0.02	0.12	0.11	0.28	0.09
Toluene	0.19	0.67	0.09	0.07	0.26	0.11	1.02	0.91	0.88	0.14
Carbon Dioxide	48.55	49.99	50.15	48.85	48.91	49.13	52.05	48.29	48.03	49.71
Oxygen	50.17	50.09	50.49	50.37	50.06	51.12	48.11	51.11	50.78	51.09
Nitrogen	50.13	50.22	52.82	50.66	50.16	50.02	50.92	50.01	50.08	48.79

Table 7
METHOD DETECTION AND QUANTIFICATION LIMITS FOR HYDROCARBONS IN NATURAL GAS

Analyte	s* (ppmv)	LOD (ppmv) LOD= 0 + 3 x s	LOQ (ppmv) LOQ= 0 + 10 x s
Methane	0.421	1.26	4.21
Ethane	0.414	1.24	4.14
Propane	0.369	1.11	3.69
Isobutane	0.319	0.96	3.19
n-Butane	0.300	0.90	3.00
Neo-Pentane	0.267	0.80	2.67
Isopentane	0.360	1.08	3.60
n-Pentane	0.332	1.00	3.32
2.2Dimethylbutane	0.251	0.75	2.51
2.3Dimethylbutane	0.322	0.97	3.22
3Methylpentane	0.318	0.96	3.18
2Methylpentane	0.380	1.14	3.80
n-Hexane	0.246	0.74	2.46
2.4Dimethylpentane	0.289	0.87	2.89
2.2.3Trimethylbutane	0.322	0.96	3.22
2Methylhexane	0.316	0.95	3.16
3Methylhexane	0.240	0.72	2.40
3ethylpentane	0.320	0.96	3.20
n-Heptane	0.294	0.88	2.94
Isooctane	0.297	0.89	2.97
n-Octane	0.385	1.16	3.85
Methylcyclohexane	0.271	0.81	2.71
Cyclohexane	0.064	0.19	0.64
Benzene	0.081	0.24	0.81
Toluene	0.388	1.16	3.88

*s = standard deviation of the concentrations measured and collected in table 2

material with the composition: 50 ppm CO_2, 50 ppm O_2, 50 ppm N_2 in Helium balance. The results obtained after 10 consecutive injections of the sample and the values of standard deviation, limit of detection and quantification are collected in tables 6-8. The detection limits of hydrocarbons resulted to be between 0.19 and 1.26 ppmv, which indicates a high sensitivity of the method.

Repeatability

The repeatability test (checking consistency of calculated results for the analyte peak over a short time period, by the same user, on the same instrument) was run using a natural gas sample (table 9). The relative standard deviations values range from 0.043293 to 3.673469 % giving a good repeatability of measurements.

Analyte	s* (ppmv)	LOD (ppmv) LOD= X** + 3 x s	LOQ (ppmv) LOQ= X** + 10 x s
Carbon Dioxide	1.177	52.90	61.13
Oxygen	0.890	53.01	59.24
Nitrogen	1.019	53.44	60.57

*s = standard deviation of the concentrations measured and collected in Table 2

** X= the average of concentrations obtained after 10 consecutive runs of analyte

Table 8
METHOD DETECTION AND QUANTIFICATION LIMITS FOR PERMANENT GASES IN NATURAL GAS

Table 9
METHOD REPEATABILITY

Analyte	No. of replicates	Average %Vol	s (%Vol)	RSD %
Methane	7	88.12330	0.011628	0.043293
Ethane	7	6.29980	0.005190	0.082384
Propane	7	1.60356	0.006233	0.388695
Isobutane	7	0.64319	0.003854	0.599167
n-Butane	7	0.49436	0.003794	0.767508
Neo-Pentane	7	0.01083	0.000243	2.244037
Isopentane	7	0.31616	0.003583	1.133369
n-Pentane	7	0.09934	0.000387	0.389241
2,2Dimethylbutane	7	0.03270	0.000693	2.118717
2,3Dimethylbutane	7	0.05093	0.000624	1.224729
3Methylpentane	7	0.03129	0.000441	1.410607
2Methylpentane	7	0.05066	0.000387	0.763334
n-Hexane	7	0.01839	0.000273	1.487167
2.4Dimethylpentane	7	0.00834	0.000018	0.215838
2.2.3Trimethylbutane	7	0.00811	0.000107	1.317485
2Methylhexane	7	0.00297	0.000079	2.653714
3Methylhexane	7	0.01670	0.000115	0.691437
3ethylpentane	7	0.01669	0.000157	0.943077
n-Heptane	7	0.00272	0.000010	0.367647
Isooctane	7	0.00031	0.000005	1.612903
n-Octane	7	0.00098	0.000021	2.142857
Methylcyclohexane	7	0.00049	0.000018	3.673469
Cyclohexane	7	0.02944	0.000425	1.443614
Benzene	7	0.00131	0.000009	0.687023
Toluene	7	0.00200	0.000045	2.250000
Carbon Dioxide	7	0.50513	0.005437	1.076325
Oxygen	7	0.12029	0.001835	1.525732
Nitrogen	7	1.50511	0.015426	1.024905

Table 10
ANALYSED COMPOUNDS UNCERTAINTY EVALUATION

Component	Concentration %Vol	u_2 %	u_3 %	u_4 %	u_c %	$U_{exp.}$ * %
Methane	64.06	1.13991	0.01000	0.01803	1.14092	2.28184
Ethane	10.45	3.68774	0.02002	0.05530	3.68913	7.37826
Propane	0.99	1.54639	0.02041	1.19041	1.98995	3.97990
Isobutane	0.5	1.56863	0.01961	1.13206	2.02522	4.05045
n-Butane	0.5	2.44898	0.02041	1.17827	2.82406	5.64811
Neo-Pentane	0.1	2.95918	0.05102	1.17827	3.89659	7.79317
Iso-pentane	0.1	2.70408	0.02041	1.17827	3.15995	6.31991
n-Pentane	0.1	4.28571	0.04762	2.74929	5.10683	10.21366
2.2Dimethylbutane	0.3	1.16949	0.02034	0.97856	2.61049	5.22098
2.3Dimethylbutane	0.3	0.37097	0.01935	1.86242	2.25977	4.51954
3Methylpentane	0.3	7.24138	0.05172	1.99086	7.64157	15.28314
2Methylpentane	0.3	15.58442	0.04870	1.49961	15.67507	31.35014
n-Hexane	0.25	10.20408	0.05102	1.17827	10.37911	20.75821
2.4Dimethylpentane	0.25	20.17717	0.04921	0.90921	20.19885	40.39771
2.2.3Trimethylbutane	0.2	10.76923	0.05128	1.48039	10.95017	21.90034
2Methylhexane	0.2	14.28571	0.04762	2.74929	14.78799	29.57598
3Methylhexane	0.2	10.00000	0.04348	7.53066	12.53757	25.07515
3ethylpentane	0.2	10.45455	0.04545	5.24864	11.73615	23.47230
n-Heptane	0.2	11.05263	0.05263	3.03869	11.46920	22.93839
Isooctane	0.1	11.11111	0.05556	6.41500	12.93629	25.87257
n-Octane	0.1	15.00000	0.04545	5.24864	16.02927	32.05854
Methylcyclohexane	0.1	11.00917	0.04587	4.76711	12.54033	25.08066
Cyclohexane	0.1	16.66667	0.05556	6.41500	17.91696	35.83393
Benzene	0.05	11.70213	0.05319	3.68521	12.28750	24.57499
Toluene	0.05	12.72727	0.04545	5.24864	13.94608	27.89216
Carbon Dioxide	5	1.01010	0.01010	0.58318	1.58713	3.17426
Oxygen	5	0.19841	0.00992	0.45821	1.60539	3.21078
Nitrogen	10	2.08333	0.01984	0.45821	2.36666	4.73331

* $U_{exp.}$ – expanded uncertainty, $U_{exp}=2 \times u_c$

Uncertainty evaluation

The method validation involves, beside the verification of performance characteristics, also the identification of factors that influence these characteristics and the grade of influence, namely the estimation of measurement uncertainty. Uncertainty evaluation represents an important part of the validation plan. All sources of uncertainty were identified, while the uncertainties budget was established.

Values of standard uncertainties were obtained from calibration certificates and method repeatability tests. The combined uncertainty was calculated according to the equation (2):

$$u_c = \sqrt{u_1^2 + u_2^2 + u_3^2 + u_4^2} \quad (2)$$

where: u_1 is the uncertainty associated to repeatability (the values are presented in table 9); u_2 is the uncertainty associated to instrument calibration; u_3 is the uncertainty associated to standards and u_4 is the uncertainty associated to measurement accuracy.

The cover factor used for the measurements is k=2, as normal distribution of errors, and 95% confidence level conditions were considered. The results demonstrate that the method can be used for the determination of C1-C8 hydrocarbons, carbon dioxide, oxygen and nitrogen in natural gas composition. Calculated values are presented in table 10.

After evaluating the data from table 10, it was found that the secondary components of natural gas present an uncertainty significantly higher than the main components due to lower measurement range.

Conclusions

A sensitive and accurate chromatographic method for separation and quantification of hydrocarbons and permanent gases in natural gas was developed. The detection of all components was possible within 32 min using flame ionization and thermal conductivity detectors. The method was declared selective, the relative standard deviations of the retention times being smaller than 0.5% in all the cases.

The method was validated over the typical concentration range of hydrocarbons, oxygen, nitrogen and carbon dioxide found in natural gas.

It offers good accuracy and precision for determination of hydrocarbons (C1-C8) and permanent gases (O_2, N_2, CO_2) in natural gas samples. The range of linearity makes this method suitable for natural gas analysis, the correlation coefficients ranging between 0.995334 and 0.999996. Repeatability tests showed that the relative standard deviations do not exceed 3.68%.

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References

1. SHIMEKIT, B., MUKHTAR, H., Natural Gas Purification Technologies – Major Advances for CO_2 Separation and Future Directions, Advances in Natural Gas Technology, InTech, edited by Dr. Hamid Al-Megren , 2012, p. 235
2. BAHADORI, A., MOKHATAB, S., Journal of Natural Gas Chemistry, **41,** No. 4, 2007, p. 349
3. LEE, Y. H., LEE, D. W., KIM, H., CHOI, H. S., LEE, K. Y., Fuel, **159**, 2015, p. 259
4. SALKUYEH, Y. K., ADAMS, T. A., Energy Conversion and Management, **74**, 2013, p. 492
5. BOMBOS, D., BOMBOS, M., ROSCA, P., VASILIEVICI, G., GHIUREA, M., Rev. Chim.(Bucharest), **62**, no. 9, 2011, p. 911
6. ASAFTEI, I. V., EARAR, K., BIRSA, L. M., SANDU, I.G., LUNGU, N. C., SANDU, I., Rev. Chim. (Bucharest), **66**, no. 7, 2015, p. 963
7. JARRAHIAN, A., HEIDARYAN, E., Fuel, **134**, 2014, p. 333
8. LIU, K., ZHANG, B. J., CHEN, Q. L., Energy Procedia, **75**, 2015, p. 2015
9. SUN, C., WEN, B., BAI, B., Chemical Engineering Science, **138**, 2015, p. 616
10. DINU, G. F., DUMITRESCU, V., Rev. Chim.(Bucharest), **60**, no. 10, 2009, p. 1061
11. OHS, B., LOHAUS, J., WESSLING, M., Journal of Membrane Science,**498**, 2016, p. 291
12. ROUSSANALY, S., ANANTHARAMAN, R., LINDQVIST, K., Journal of Natural Gas Science and Engineering, **20**, 2014, p.38
13. EPARU, C., ALBULESCU, M., NEACSU, S., ALBULESCU, C., Rev. Chim.(Bucharest), **65**, no. 11, 2014, p. 1385
14. DEMIRBAS, A., Methane Gas Hydrate – Natural Gas, Springer, 2010, p. 57-76
15. LUONG, J., GRAS, R., CORTES, H. J., SHELLIE, R., A., Journal of Chromatography A, **1271**, 1, 2013, p. 185
16. WEIJUN, Y., Journal of Chromatography A, **1167**, 2007, p. 225
17. SAITO, H., SUZUKI, N., TAKAHASHI, K. U., Geochemical Journal, **46**, 2012, p. 255
18. KIM, S. H., NAM, S. M., KOH, K. O., CHOI, Y. W., Bull. Korean Chem. Soc., **20**, No. 7, 1999, p. 843
19. LECHNER-FISH, T. J., LUND, M. J., RYDER, S. L., Am. Lab., **24**, 15, 1994, p. 288
20. LECHNER-FISH, T. J., Am. Lab., **28**, 16, 1996, p. 37
21. MAGNUSSON, B.,ORNEMARK, U. (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, 2nd ed. 2014
22. MINCA, I., BAJENARU, I., GURAN, C., JOSCEANU, A.M., ISOPESCU, R. D., Rev. Chim.(Bucharest), **66**, no. 6, 2015, p. 759

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