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Design and Evaluation of A Capillary GC Analyzer for Automated Simultaneous Analysis of Permanent Gases and Light Hydrocarbons in Natural Gases

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ABSTRACT

In this paper we focus on the design and evaluation of a natural gas analyser that meets the demands of a preliminary draft of the standard DIN 51872.T5 of September 1992 for Germany. The dual oven, multicolumn GC system allows the simultaneous analysis of permanent gases such as helium, hydrogen,oxygen nitrogen carbon dioxide and carbon monoxyde and hydrocarbons with 2 up to 8 carbon atoms, within 40 minutes.

The analyzer consists of two independently operating GC systems. Their series coupled sample transfer line permits the simultaneous purging and introduction of both samples in the respective systems. The sample introduction is performed by gas sampling valves equipped with a sample loop.

Permanent gases, CO, CO_2, as well as methane and C_2-hydrocarbons are analysed in the first GC, by means of two capillary PLOT columns. The column switching device in between these columns consists of two multiport rotating micro valves. The detection system is a series coupled combination of a low volume thermal conductivity detection (TCD) and flame ionisation detection (FID). A methanizer in between both detectors allows simultaneous TCD and FID detection of carbon monoxide and carbondioxide.

INTRODUCTION

The calculation of the calorific value or the hydrocarbon dew point requires detailed and accurate analysis of natural gas, as can be achieved by gas chromatographic analysis. Several attempts aiming accurate natural gas analysis have been described in the literature.

In this study we focus on the design and evaluation of a natural gas analyzer that meets the demands of a preliminary draft of the standard DIN 51872.T5 for Germany. As laid down in this proposal the application of 3 capillary columns and sample introduction by means of multiport microvalves equiped with a sample loop is required. A methanizer in between the TCD and FID detector is prescribed, in order to permit detection of CO_2 and CO with both detectors.

The natural gas analyzer presented in this paper consists of two independently operating GC-instruments. The sample introduction in both these instruments is synchronised, so that simultaneous flushing of the sample valves as well as the successive introduction of both samples on the respective columns is achieved.

EXPERIMENTAL

Instrumentation. An overall schematic design of the system is presented in **Figure 1**.

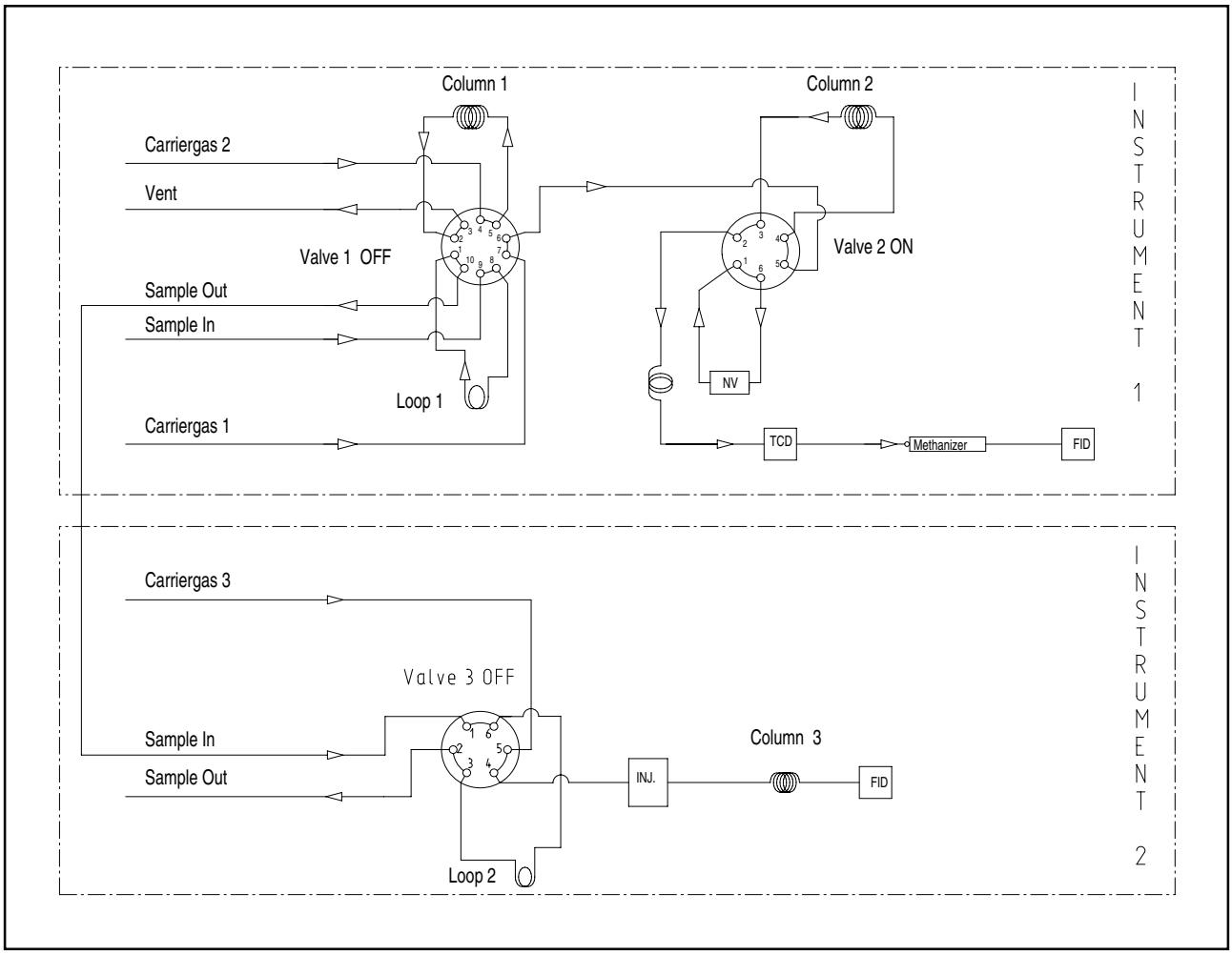

Figure 1. *Overall schematic design of the heart of the analyzer. Mode: "stand by" or analysis of the components present in column 2 or flushing of the sample loops of both instruments and backflush of column 1.*

Columns:

1: 25 m Poraplot U, d_i. = 0.53 mm d_f = 20µm
(Chrompack, Middelburg, The Netherlands).

2: 50 m Molsieve 5Å, d_i = 0.53 mm d_f = 50µm
(Chrompack, Middelburg, The Netherlands).

3: 60 m DB-1, d_i = 0.32 mm d_f = 5µm
(J&W, Folsom, CA, USA)

Valves: Instrument 1: 6-port valve, 10-port valve
Instrument 2: 6-port valve
(VALCO / VICI AG, Schenkon Switzerland)

Operation. In the first instrument all the permanent gases, CO, CO_2, CH_4, ethylene and ethane are analysed. The components are selectivly transfered to the different columns and thereafter to the TCD and /or FID detector. It consists of a Hewlett Packard 5890 II, two capillary plot columns, which are connected via a ten-port and a six-port microvalve. The sample loop is connected to the ten-port valve and provided with a Graphpack "Direktanschluß" injector (Gerstel GmbH, Mülheim, Germany). For the detection, both a TCD and a FID detector, interfaced by a methanizer are available. In this way, CO and CO_2 can be detected in the TCD, but also in the FID, after reduction to CH_4 in the methanizer. All the saturated and unsaturated hydrocarbons with 3 or more carbon atoms are analysed in the second instrument, exclusively using FID detection. This part of the analyzer consists of a Hewlett Packard 5890 II gaschromatograph with a combination of a microvalve actuated sample loop and a standard split/splitless injector, an FID detector and a wide-bore thick film non polar fused silica column.

System Modes.

1. Stand by, backflush of column 1, flushing of the sample loops and analysis of the components present in column 2 (valve1 = off, valve2 = on, valve3 = off).
2. Sample introduction and selective transfer of the permanent gases, CO and CH_4 from column 1 to column 2 (valve1 = on, valve2 = on, valve3 = on).
3. Storing of these components in column 2 and analysis of the residual components left in column 1 (valve1 = on, valve2 = off, valve3 = on).
4. Backflush of column 1 and analysis of the components stored in column 2 (valve1 = off, valve2 = on, valve3 = on)

RESULTS AND DISCUSSION

The expected concentration ranges for the respective components as well as the intentional repoducibility is given in **Table I**.

Component	Order of concentration range [Mol %]	Order of intentional reproducibility [rel % STD]
He	≈0.05	1
CO_2	0.1 - 5	0.4
N_2	0.2 - 17	0.2
O_2	0.001 - 2	0.5
H_2	0.001 - 5	0.5
CO	0.001 - 0.5	0.5
CH_4	75-98	0.1
C_2H_6	0.5 - 10	0.4
C_2H_4	≈0.01	0.4
C_3H_8	0.05 - 4	0.5
C_3H_6	≈0.001	0.5
C_4H_{10}	≈0.1	1
C_5H_{12}	≈0.03	2
C_6H_{12} - $C_{10}H_{22}$	≈0.001 - ≈0.02	5

Table I. *Expected concentration ranges and intentional reproducibility.*

For the optimization and valuation of the performance of the natural gas analyzer, two different gas mixtures have been used. Any estimation of the qualitative and quantitative composition of natural gas mixtures is given in **Table II**.

Component	Concentration [Mol %]	
	Mix 1	Mix 2
Helium	0.043	0.004
Carbondioxide	1.257	1.761
Nitrogen	10.57	0.758
Hydrogen	< 0.001	2.194
Oxygen	0.010	0.028
Methane	82.87	82.69
Carbonmonoxide	-------	0.200
Ethane	3.986	8.498
Ethylene	-------	0.063
Propane	0.872	0.700
Propylene	-------	0.007
i-Butane	0.110	0.296
n-Butane	0.168	0.596
neo-Pentane	0.005	0.002
i-Pentane	0.030	0.084
n-Pentane	0.030	0.087
Hexane	0.031	0.039
Heptane	0.009	0.008
Octane	0.002	0.001
Nonane	0.001	0.002
Benzene	0.012	0.002
Toluene	0.002	0.001

Table II. *Qualitative and quantitative composition of the test mixtures.*

Representative chromatograms for both natural gas test mixtures analysed with instrument 1 and instrument 2 are presented in **Figure 2 - 7**.

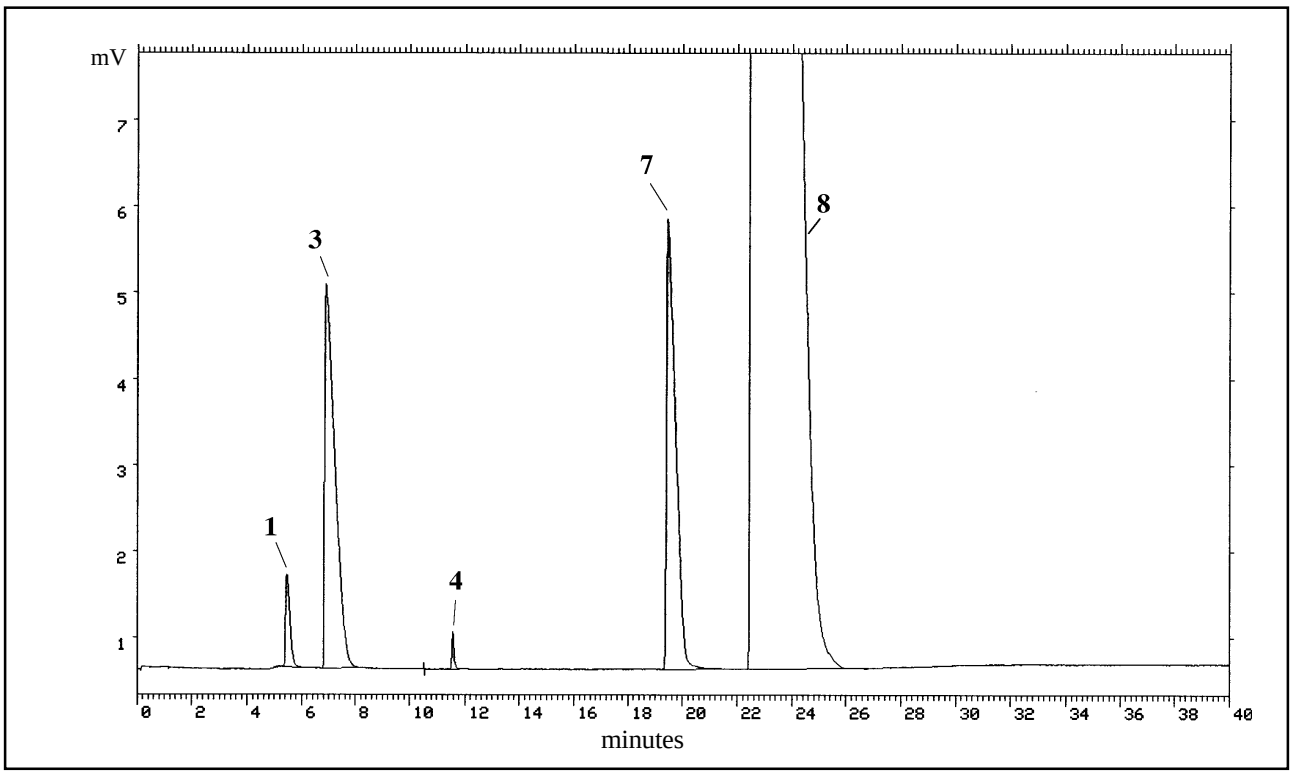

Figure 2. *TCD-chromatogram of test mixture 1.*
Peak No.: **1** = CO_2; **3** = C_2H_6; **4** = He; **7** = N_2; **8** = CH_4;
t = 10.5 min: Start of analysis of components, stored in column 2, instrument 1.

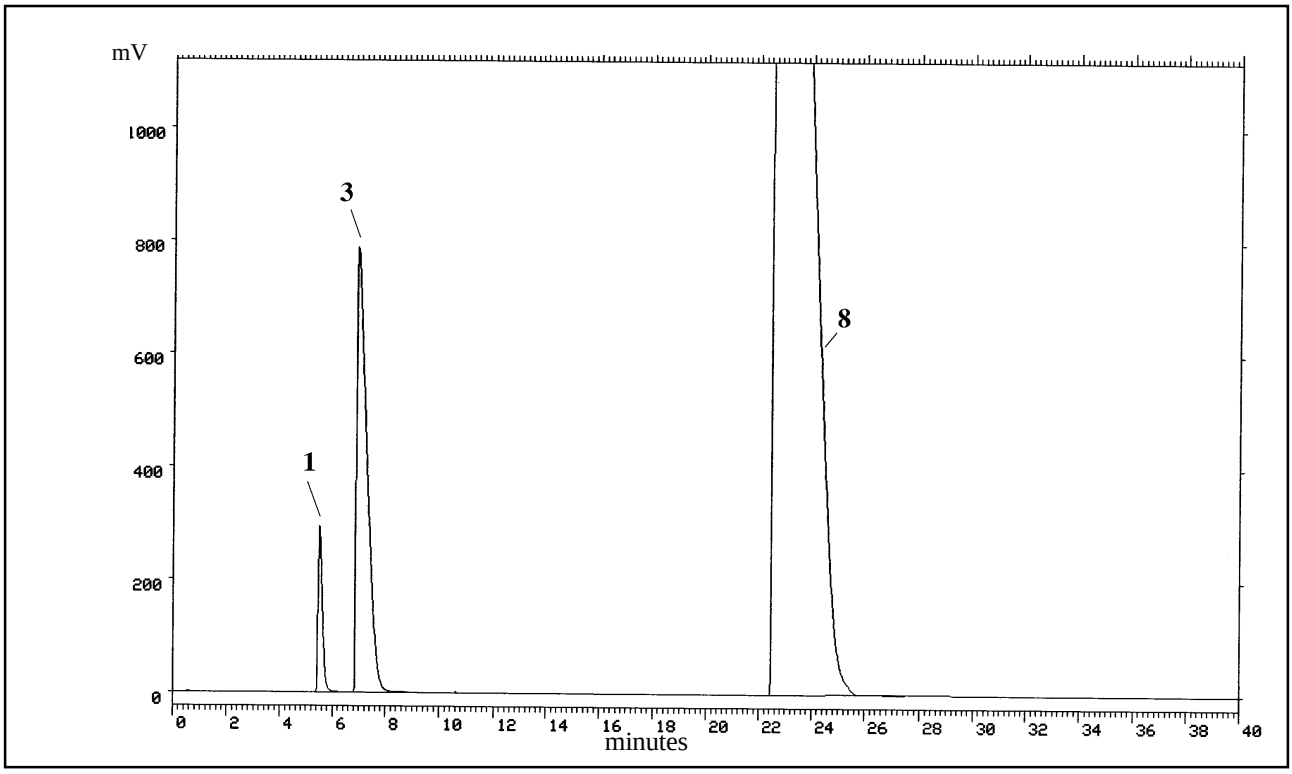

Figure 3. *FID-chromatogram of test mixture 1.*
Peak No.: **1** = CO_2; **3** = C_2H_6; **8** = CH_4;
t = 10.5 min: Start of analysis of components, stored in column 2, instrument 1.

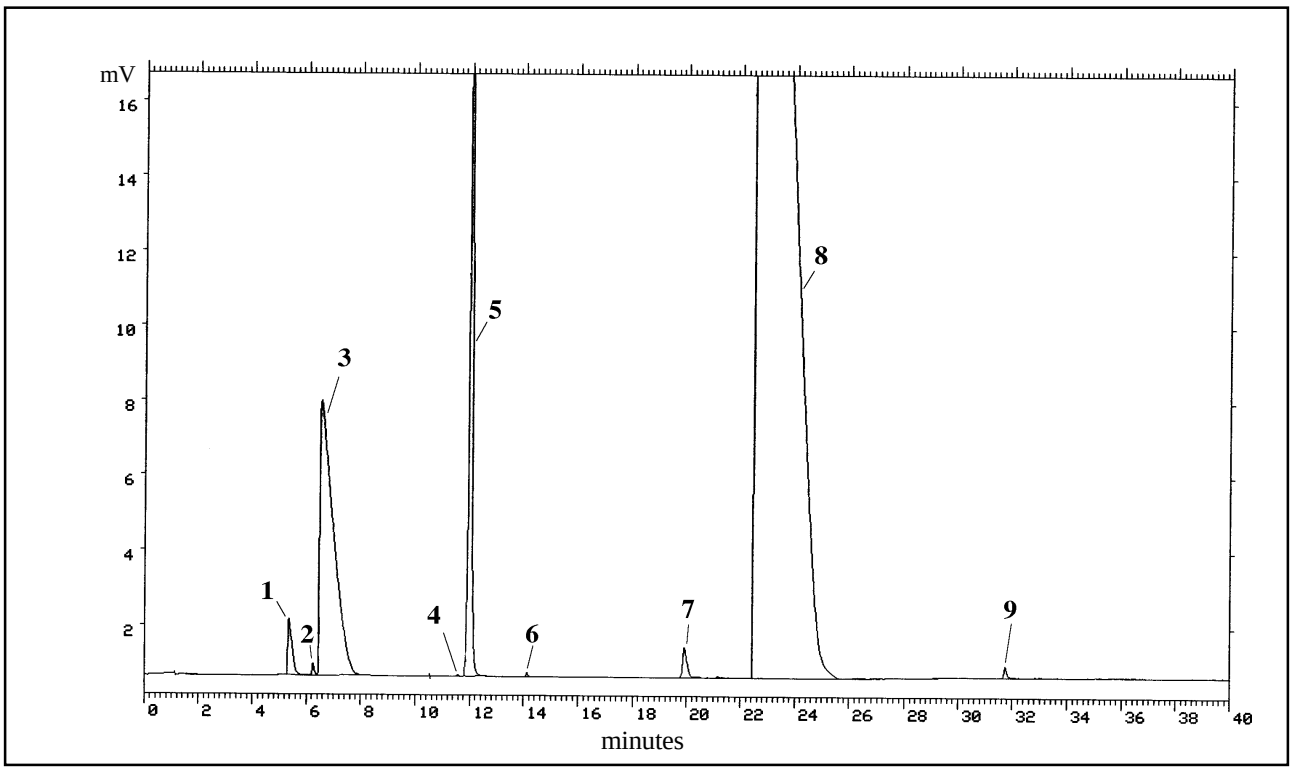

Figure 4. *TCD-chromatogram of test mixture 2.*
Peak No.: **1** = CO_2; **2** = C_2H_4; **3** = C_2H_6; **4** = He; **5** = H_2; **6** = O_2; **7** = N_2; **8** = CH_4; **9** = CO;

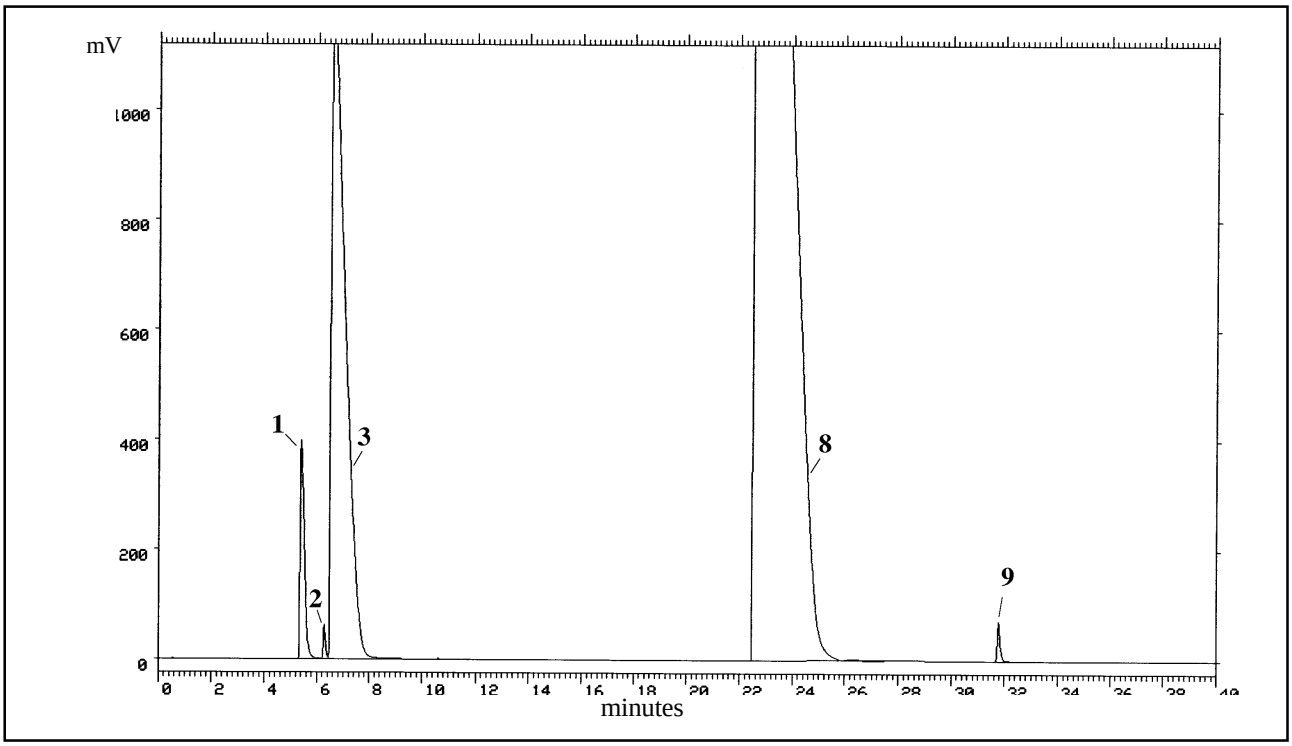

Figure 5. *FID-chromatogram of test mixture 2.*
Peak No.: **1** = CO_2; **2** = C_2H_4; **3** = C_2H_6; **8** = CH_4; **9** = CO;

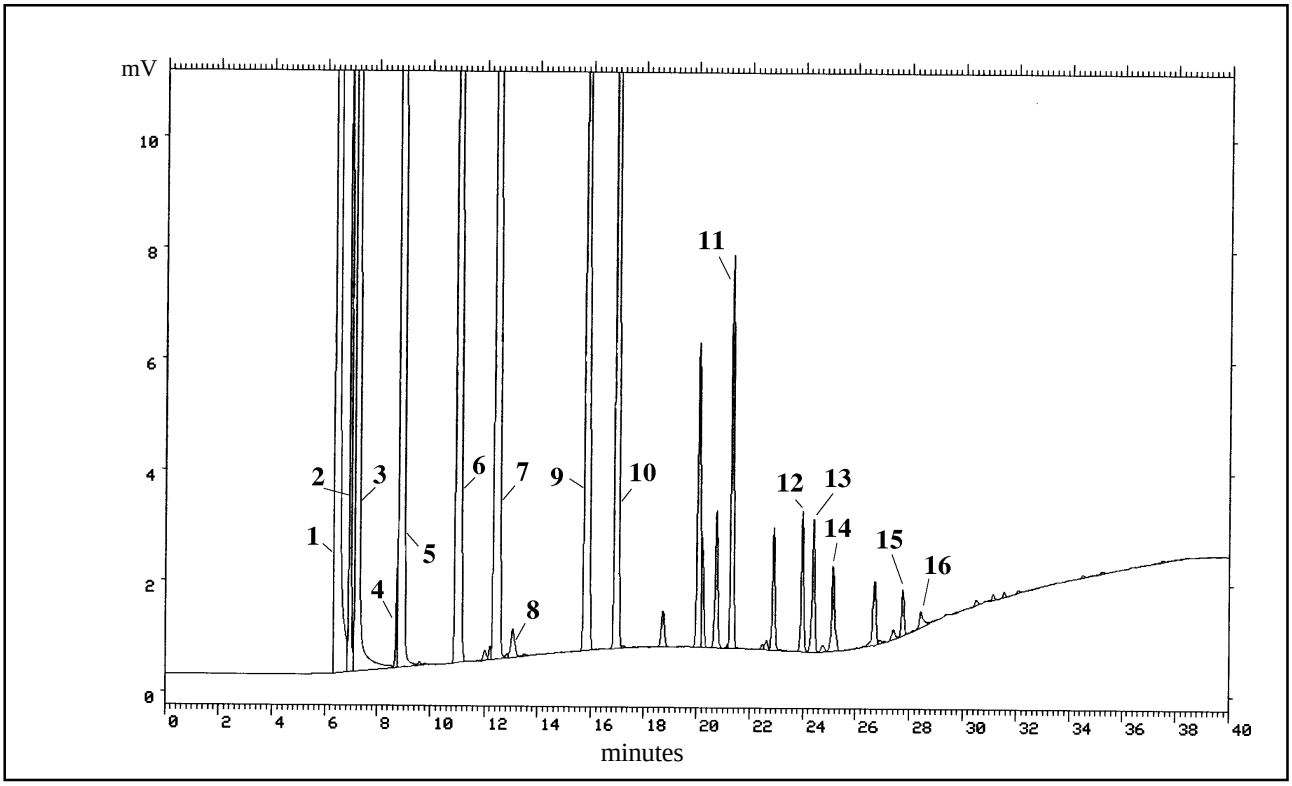

Figure 6. *FID-chromatogram of test mixture 2 analysed with instrument 2.*
Peak No.: **1** = CH_4; **2** = C_2H_4; **3** = C_2H_6; **4** = C_3H_6; **5** = C_3H_8; **6** = i-C_4H_{10};
7 = n-C_4H_{10}; **8** = neo-C_5H_{12}; **9** = i-C_5H_{12}; **10** = n-C_5H_{12}; **11** = n-C_6H_{14};
12 = benzene; **13** = cyclohexane; **14** = n-C_7H_{16}; **15** = toluene; **16** = C_8H_{18};

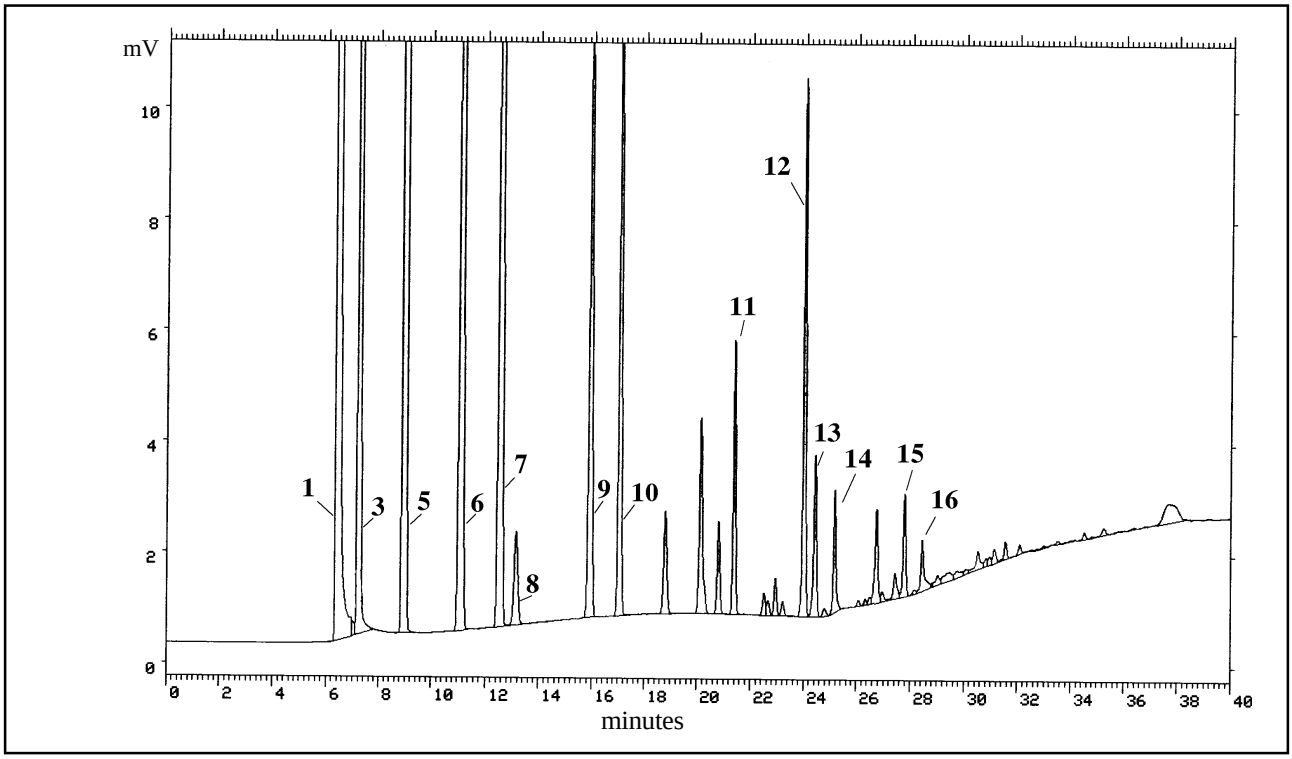

Figure 7. *FID-chromatogram of test mixture 1 analysed with instrument 2.*
Peak No.: Cf. **Figure 6**.

Comparing **Figure 2 and 3,** and **4 and 5**, obviously the amplification factor (= ratio of the FID and TCD signal) obtained by the methanizer is about 150. That this amplification factor is of the same order as for ethane, indicates a quantitative conversion of CO_2 to CH_4. Comparing **Figure 4 and 5** it can be seen that the amplification factoras well as the conversion factor for CO is of the same order as for CO_2.

CONCLUSION

It can be concluded:

1. that the first critical peak couple (C_2H_4 and C_2H_6) are not sufficiently separated in instrument 2. Therefore they have to be separated and quantified in instrument1. Propene and propane however are acceptably separated in instrument 2.
2. From extensive reproducibility tests with both mixtures it appeared that the intended reproducibility, as summarized in **Table I**, has been achieved for all the conponents in both parts of the natural gas analyzer.

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