



BSI Standards Publication

**Petroleum industry and products — Determination of composition of refinery heating gas and calculation of carbon content and calorific value — Gas chromatography method**

**National foreword**

This British Standard is the UK implementation of EN 15984:2011.

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**Petroleum industry and products - Determination of composition  
of refinery heating gas and calculation of carbon content and  
calorific value - Gas chromatography method**

Industries et produits pétroliers - Détermination de la  
composition des gaz combustibles de raffinerie, de leur  
pouvoir calorifique et de leur teneur en carbone - Méthode  
par chromatographie en phase gazeuse

Mineralölindustrie und -produkte - Bestimmung der  
Zusammensetzung von Heizgas für Raffinerien und  
Berechnung des Kohlenstoffgehaltes und des Heizwertes -  
Gaschromatographisches Verfahren

This European Standard was approved by CEN on 9 March 2011.

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## Foreword

This document (EN 15984:2011) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2011, and conflicting national standards shall be withdrawn at the latest by October 2011.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document is based on a DIN Standard [3] with the same scope.

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## 1 Scope

This European Standard defines a gas chromatographic analysis for the determination of the composition of fuel gases, as used in refinery heating gas. These results are used to calculate the carbon content and the lower calorific value.

With this gas chromatographic analysis, an overall of 23 refinery heating gas components are determined in concentrations as typically found in refineries (see Table 1 for further details).

Water is not analysed. The results represent dry gases.

NOTE 1 Depending on the equipment used, there is a possibility to determine higher hydrocarbons as well.

NOTE 2 For the purposes of this European Standard, the terms “% (V/V)” is used to represent the volume fraction ( $\varphi$ ).

**IMPORTANT — This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations.**

## 2 Principle

This standard defines a procedure that is used to determine all components that are present in a typical refinery heating gas, as indicated in Table 1.

NOTE The composition range in which each component can be analyzed does depend on the actual sample composition as higher amounts of a certain component may affect the detection range of other components eluting close by. The general ranges which apply to all the individual components are:

- Hydrocarbons from 0,01 (mol/100 mol) up to 100 (mol/100 mol);
- Non-condensable gases from 0,02 (mol/100 mol) up to 100 (mol/100 mol);
- For hydrogen sulfide a range between 0,1 (mol/100 mol) up to 10 (mol/100 mol) has been found applicable.

Three different analysis systems are necessary; they may be built in three separate gas chromatographs, or be integrated into one.

Depending on the configuration, hydrocarbons with more than five carbon atoms are reported as a sum parameter. The composition of the refinery heating gas is used to calculate the carbon content and the calorific value. A typical procedure is described hereafter. A configuration is acceptable when the determination gives the precision as described in Clause 9.

## 3 Reagents and materials

### 3.1 Gases.

**3.1.1 Hydrogen**, with a minimum purity of 99,995 % (V/V).

**3.1.2 Helium**, with a minimum purity of 99,995 % (V/V).

**3.1.3 Nitrogen**, with a minimum purity of 99,995 % (V/V).

**3.1.4 Air**, free of oil and water.

**3.1.5 Argon**, as alternative for analysis system 2, with a minimum purity of 99,995 % (V/V).

### 3.2 Calibration sample.

A certified reference gas mixture in concentrations that allow the determination of the necessary response factors (see 6.1) and retention times is required.

**Table 1 — Refinery heating gas components**

Number	Description	Chemical formula
1	Hydrogen	H <sub>2</sub>
2	Oxygen/Argon	O <sub>2</sub> /Ar
3	Nitrogen	N <sub>2</sub>
4	Carbon monoxide	CO
5	Carbon dioxide	CO <sub>2</sub>
6	Hydrogen sulfide	H <sub>2</sub> S
7	Methane	CH <sub>4</sub>
8	Ethane	C <sub>2</sub> H <sub>6</sub>
9	Ethene	C <sub>2</sub> H <sub>4</sub>
10	Ethyne (Acetylene)	C <sub>2</sub> H <sub>2</sub>
11	Propane	C <sub>3</sub> H <sub>8</sub>
12	Propene	C <sub>3</sub> H <sub>6</sub>
13	Propyne (Methylacetylene)	C <sub>3</sub> H <sub>4</sub>
14	Propadiene	C <sub>3</sub> H <sub>4</sub>
15	<i>iso</i> -Butane	C <sub>4</sub> H <sub>10</sub>
16	<i>n</i> -Butane	C <sub>4</sub> H <sub>10</sub>
17	<i>trans</i> -2-Butene	C <sub>4</sub> H <sub>8</sub>
18	1-Butene	C <sub>4</sub> H <sub>8</sub>
19	2-Methyl-Propene	C <sub>4</sub> H <sub>8</sub>
20	<i>cis</i> -2-Butene	C <sub>4</sub> H <sub>8</sub>
21	1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>
22	<i>iso</i> -Pentane	C <sub>5</sub> H <sub>12</sub>
23	<i>n</i> -Pentane	C <sub>5</sub> H <sub>12</sub>
24	Other components with 5 or more Carbon atoms, excluding <i>iso</i> - and <i>n</i> -Pentane (C <sub>5+</sub> )	

## 4 Apparatus

### 4.1 Usual laboratory apparatus and glassware.

**4.2 Gas chromatographic apparatus**, consisting of at least three separation systems able to work simultaneously in one gas chromatograph, with a Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) that should be available, and confirming to the requirements as given in Clause 5.

## 5 Gas chromatographic analysis

### 5.1 Analysis systems

The gas chromatographic system consist of the following three parts:

#### 1) Analysis system 1

All components except hydrogen (see Table 1) are retained on a porous polymer and a molecular sieve column and back flushed.

NOTE HayeSep<sup>®</sup> and Molsieve<sup>®</sup> are examples of such commercially available columns.

Hydrogen is determined on a TCD with nitrogen (3.1.3) as the carrier gas (see Figure A.4).

#### 2) Analysis system 2

The second analysis system separates non-condensable gases, carbon dioxide, and hydrocarbons with two carbon atoms and hydrogen sulfide with helium (3.1.2) as the carrier gas and a TCD as a detector. After a pre-separation on a porous polymer column (column 3) propane and higher hydrocarbons are back flushed and vented. See Figure A.5 for details..

When the inert gases (O<sub>2</sub>/Ar, N<sub>2</sub>, CH<sub>4</sub> and CO) are on the molecular sieve 13X column, this column is isolated. Carbon dioxide, the C<sub>2</sub>-hydrocarbons and hydrogen sulfide are eluted from the porous polymer column (column 4) and are detected. The C<sub>2</sub>-hydrocarbons from this fraction are not used for quantification. After this the molecular sieve 13X column (column 6) is eluted and the components are determined on the TCD. Methane is quantified on Analysis System 3.

#### 3) Analysis system 3

The third analysis system separates and quantifies all hydrocarbons by an FID and hydrogen (3.1.1) or helium (3.1.2) as the carrier gas. Two columns are used in series. From the methyl silicone column (column 1), the components above a certain cut point e.g. *n*-pentane are back flushed and determined as a summed peak. The hydrocarbons from the alumina oxide column, column 2, are then separated and quantified. See Figure A.6 for details.

### 5.2 System configuration

The gas chromatographic system may consist of one or more gas chromatographs, with the possibility for isothermal or temperature programmed runs or both depending on the selected system configuration. A TCD and an FID shall be available.

A gas flow control system and gas sampling valves and switching valves are used.

Means for quantification shall be provided.

NOTE Optionally a vaporizer may be used.

### 5.3 Columns

A combination of packed and capillary columns is possible.

It shall be ascertained that a quantitative separation of all the components that need to be determined (see Table 1) is possible and that the summed total of C<sub>5+</sub> is quantitative. Adequate separation is required between the components on all three separation systems.

If cyclopropane can be determined, it shall be summed to propene.

An example for a typical configuration is given in Annex A.



## 6 Calibration

### 6.1 General

Depending on the production procedure of the reference gas mixture, it might be necessary to convert the concentration units of the components in the calibration gas to (mol/mol) %.

Linearity of the detectors shall be checked according to Annex B.

If calibration is necessary, e.g. daily or for an analysis series, a reference gas mixture shall be analysed. For each analysis system (see 5.1) at least one component, the reference component, needs to be calibrated. For example, for analysis system 1 hydrogen, for analysis system 2 nitrogen and for analysis system 3 propane. With these three components, an external calibration is done. The absolute response factor is calculated.

For all the other components, relative response factors will be used (see 6.3).

The relative response factor of the reference component will be set at 1,0.

As alternative all absolute response factors can be determined for all the components that need to be analyzed in a reference gas mixture. A check of this calibration can take place with a gas mixture with fewer components.

### 6.2 Absolute response factors

The determination of absolute response factors is possible when a repeatable injection is possible under constant analysis conditions. The ratio between concentration and peak area is determined and the absolute response factor is calculated with the following equation:

$$RF_i = \frac{x_i}{A_i} \quad (1)$$

where

$RF_i$  is the absolute response factor of component  $i$  ;

$x_i$  is the concentration of component  $i$  in (mol/100 mol) in the calibration gas;

$A_i$  is the peak area of component  $i$  in the calibration gas.

### 6.3 Relative response factors

For quantification relative response factors can be used too. In one analysis system, one component is used as a reference (reference component).

The relative response factor is calculated with the following equation:

$$RRF_i = \frac{RF_i}{RF_{St}} \quad (2)$$

where

$RRF_i$  is the relative response factor of component  $i$  ;

$RF_i$  is the absolute response factor of component  $i$ ;

$RF_{St}$  is the absolute response factor of the reference component  $St$ .

## 7 Calculation

### 7.1 General

For the calculation of parameters of gas mixtures, as described in this standard, the molar composition of the gas mixture is necessary.

NOTE A more accurate result may be obtained by analyzing the C5 olefins separately and not adding them to the sum of all heavier components.

### 7.2 Calculation of the non normalized mole fractions

The concentrations of the components,  $x_{i, sample}$ , mentioned in Table 1 are calculated as mole fractions. The calculation of these follows Equation (3):

$$x_{i, sample} = A_{i, sample} \times RRF_{i, St} \times RF_{StK} \quad (3)$$

where

$A_{i, sample}$  is the area of component  $i$  in the sample;

$RRF_{i, St}$  is the relative response factor of component  $i$  relative to the reference component  $St$ ;

$RF_{StK}$  is the absolute response factor of the reference component  $St$  in the reference gas mixture  $K$ .

NOTE If only absolute response factors are used, then reference component  $St$  and component  $i$  are identical. Therefore, in Equation (3)  $RRF = 1$  and each  $RF$  represents the individual component  $i$ .

### 7.3 Validation of normalized composition (reference components)

The results can be normalized, when the sum of all the mole fractions of the components are not smaller than 0,98 or greater than 1,02. If not, the analysis should be repeated. If the duplicate analysis does not improve this result, the calibration and the apparatus shall be checked.

Normalization is done according to:

$$x_i^* = \frac{x_{i, sample}}{\sum_{i=1}^k x_{i, sample}} * 100 \quad (4)$$

where

$x_i^*$  is the corrected concentration of component  $i$  in the sample in mol/100 mol;

$x_{i, sample}$  is the uncorrected concentration of component  $i$  in the sample;

$\sum_{i=1}^k x_{i, sample}$  is the sum of the non normalized mol fractions of the sample;

$k$  is the number of components.

#### 7.4 Calculation of carbon content

The determined and normalized concentrations of each component, calculated according to Equations (3) and (4) are independent of pressure and temperature. By multiplying the concentration of each component with their respective molar mass and normalizing the results, the (mol/100 mol) fractions are converted to (g/100 g) of gas,  $w_{x_i}^*$  according to:

$$w_{x_i}^* = \frac{x_i^* M_i}{\sum_{i=1}^k (x_i^* M_i)} * 100 \quad (5)$$

where

$x_i^*$  is the corrected concentration of the component  $i$  in the sample in (mol/100 mol);

$M_i$  is the molar mass of the component  $i$  in g/mol;

$\sum_{i=1}^k (x_i^* M_i)$  is the sum of the normalized molar fractions of the sample multiplied by the molar mass;

$k$  is the number of components.

The carbon content of the individual components,  $w_{C_i}$ , are given in Table D.1.

The calculation is according to Equation (6):

$$w_{C_i} = \frac{n_{C_i} M_C}{M_i} \quad (6)$$

where

$n_{C_i}$  is the number of carbon atoms in the component  $i$ ;

$M_C$  is the molar mass of carbon in g/mol;

$M_i$  is the molar mass of the component  $i$  in g/mol.

The sum of the values found by multiplication of the concentration  $w_i$  in (g/100g gas) with the molar carbon concentration  $w_{C_i}$  of component  $i$  results in the carbon content of the mixture (g C/100g gas),  $C_c$ .

$$C_i = \sum_{i=1}^k w_{x_i}^* \cdot w_{C_i} \quad (7)$$

## 7.5 Calculation of lower calorific value, on mass basis

The component concentration determined in 7.2 is independent of pressure and temperature. Multiplication with the molar mass in g/mol results in component quantity in grams. If the sum of the individual quantities is normalized to 100 g, then the component quantities are given in g/100 g gas.

For the conversion of the normalized mol fractions (7.3) in (g/100 g) of gas refer to 7.4.

The lower calorific values for the individual components in Table D.1 shall be used. The conversion in kJ/g is according to Equation (8):

$$H_{u_{C_i}} = \frac{H_{u_i}}{M_i} \quad (8)$$

where

$H_{u_{C_i}}$  is the lower calorific value of component  $i$  in kJ/g;

$H_{u_i}$  is the lower calorific value of component  $i$  in kJ/mol;

$M_i$  is the molar mass of component  $i$  in g/mol.

The sum of the values found by multiplication of the concentration  $w_{x_i}^*$  in (g/100 g gas) with the lower calorific value  $H_{u_i}$  of each component  $i$  in kJ/mol results in the lower calorific value of the total mixture in (kJ/100 g gas).

$$H_u = \sum_{i=1}^k w_{x_i}^* \times H_{u_{C_i}} \quad (9)$$

## 8 Expression of results

Report the carbon content in (g/100 g) of gas, to the nearest 0,01.

Report the calorific value in (kJ/100 g) of gas, to the nearest 0,01.

Report of the compositional analysis of the refinery heating gas in (mol/100 mol), to the nearest 0,01.

## 9 Precision

### 9.1 General

The precision given in 9.2 and 9.3 was determined by statistical examination of interlaboratory test results in accordance with EN ISO 4259 [1].

## 9.2 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated from the following equation only in one case in twenty.

For the lower calorific value:

$$r = 0,004 * X \text{ (kJ/100 g)} \quad (10)$$

and for the carbon content:

$$r = 0,01 * X \text{ (g/100 g)} \quad (11)$$

where

$X$  is the mean of the results being compared.

## 9.3 Reproducibility

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated from the following equation only in one case in twenty.

For the lower calorific value:

$$R = 0,022 * X \text{ (kJ/100 g)} \quad (12)$$

and for the carbon content:

$$R = 0,022 * X \text{ (g/100 g)} \quad (13)$$

where

$X$  is the mean of the results being compared.

## 10 Test report

The test report shall contain at least the following information:

- a) reference to this European Standard, i.e. EN 15984;
- b) type and complete identification of the product (sample) tested;
- c) result of the test (see Clause 7);
- d) any deviation, by agreement or otherwise, from the procedure specified;
- e) date of the test.

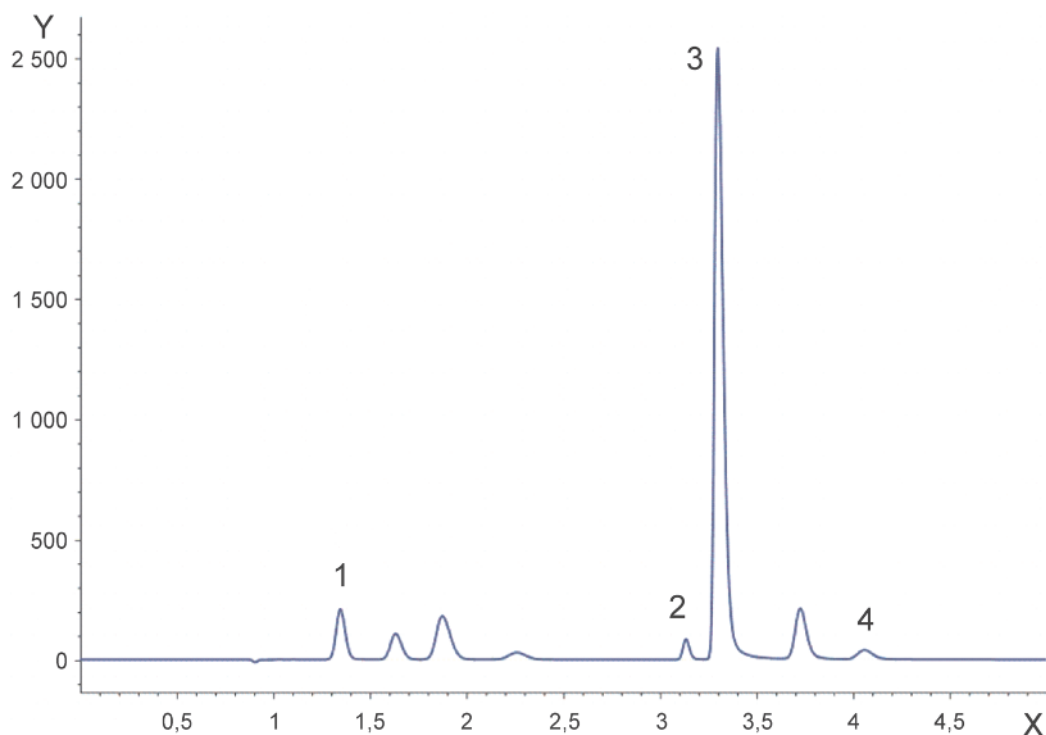
## Annex A (informative)

### Possible column combination

The following combination of columns may be used:

- Column 1 Pre column for hydrocarbons up to C6. Nominally 3 m x 320 µm methyl silicone.
- Column 2 Analysis column for hydrocarbons. Nominally 25 m x 320 µm aluminium oxide Plot.
- Column 3 Nominally 0,25 m of a porous polymer (e.g. HayeSep Q).
- Column 4 Nominally 1 m of a porous polymer (e.g. HayeSep N).
- Column 5 Nominally 2 m of a porous polymer (e.g. HayeSep Q) + Molsieve 5A. The two columns are combined in series with the porous column in front of the Molsieve column.
- Column 6 Nominally 2 m of Molsieve 13X.

An example of a resulting TCD chromatogram is given in Figure A.1.

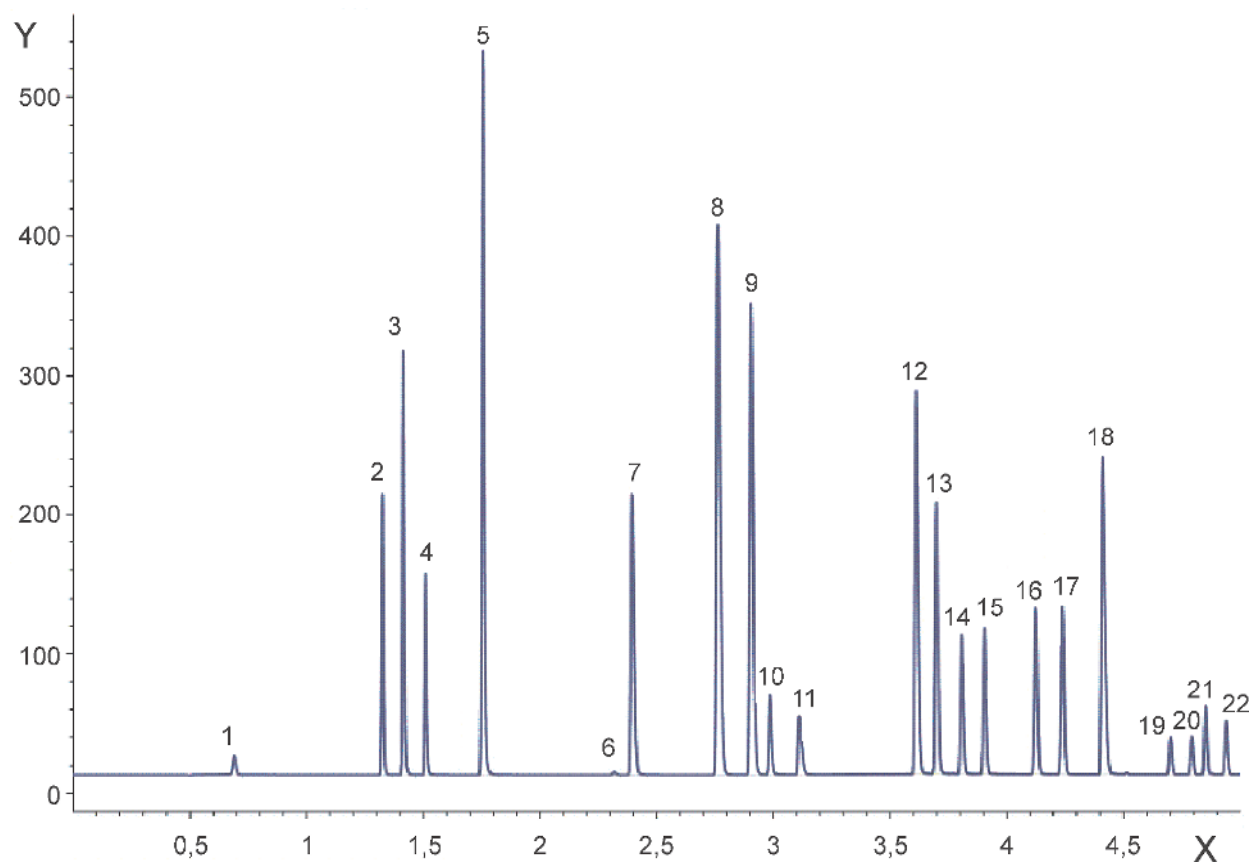


#### Key

- 1 carbon dioxide
- 2 oxygen
- 3 nitrogen
- 4 carbon monoxide
- X time (min.)
- Y output (µV)

Figure A.1 — Example of a TCD chromatogram of a reference gas

Methane, Ethane, Ethene and Acetylene are quantified by FID (see Figure A.2).

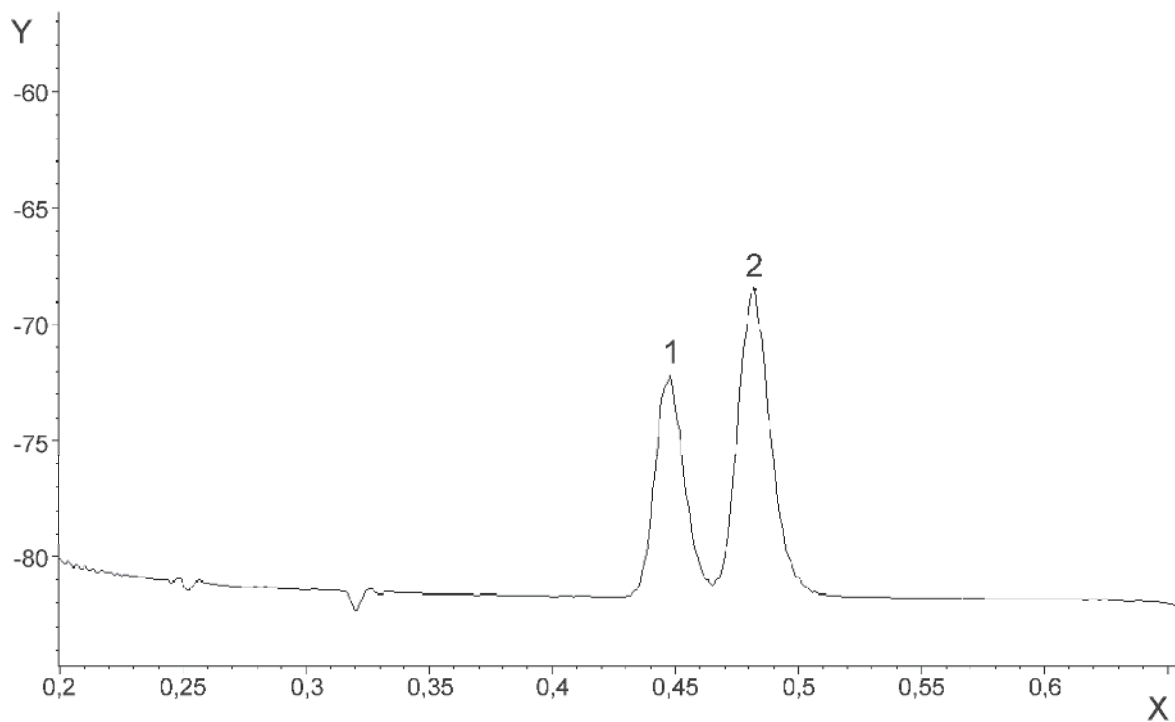


**Key**

1	C6+	10	propadiene	19	trans-2-pentene
2	methane	11	acetylene	20	2-methyl-2-butene
3	ethane	12	<i>trans</i> -2-butene	21	1-pentene
4	ethene	13	1-butene	22	<i>cis</i> -2-pentene
5	propane	14	<i>iso</i> -butene		
6	cyclopropane	15	<i>cis</i> -2-butene	X	time (min.)
7	propene	16	<i>iso</i> -pentane	Y	output (pA)
8	<i>iso</i> -butane	17	<i>n</i> -pentane		
9	<i>n</i> -butane	18	1,3-butadiene		

**Figure A.2 — Example of a FID chromatogram of a reference gas**

For the Hydrogen/Helium channel a chromatogram is given in Figure A.3.



**Key**

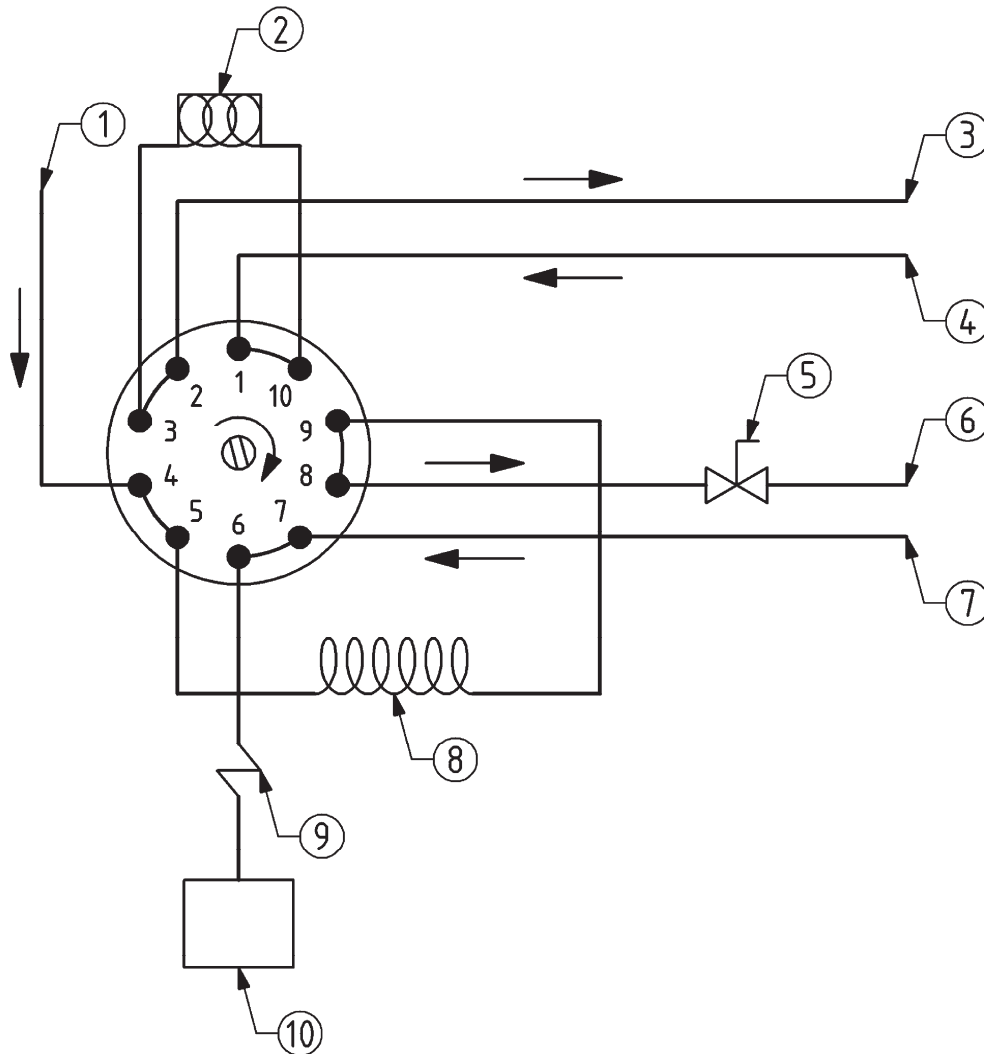
- 1 helium
- 2 hydrogen

- X time (min.)
- Y output (µV)

**Figure A.3 — Example of a H<sub>2</sub>/He chromatogram**



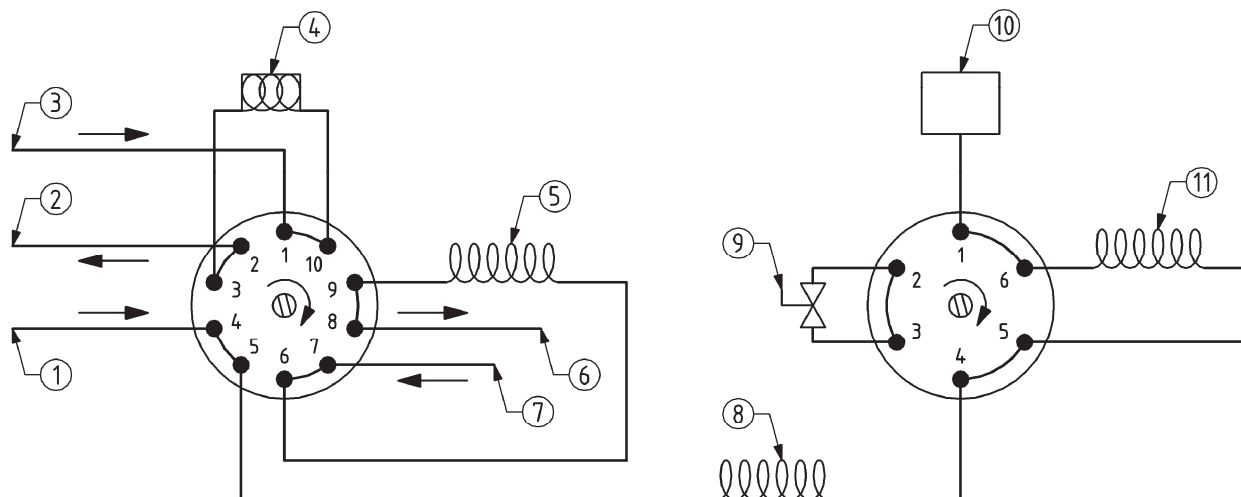
Details on the equipment for the testing of different components are given in Figures A.4, A.5 and A.6.



**Key**

- |   |                        |    |                        |
|---|------------------------|----|------------------------|
| 1 | carrier N <sub>2</sub> | 6  | vent N <sub>2</sub>    |
| 2 | sample loop            | 7  | carrier N <sub>2</sub> |
| 3 | gas sample out         | 8  | column 5               |
| 4 | gas sample in          | 9  | fixed restriction      |
| 5 | needle valve           | 10 | TCD                    |

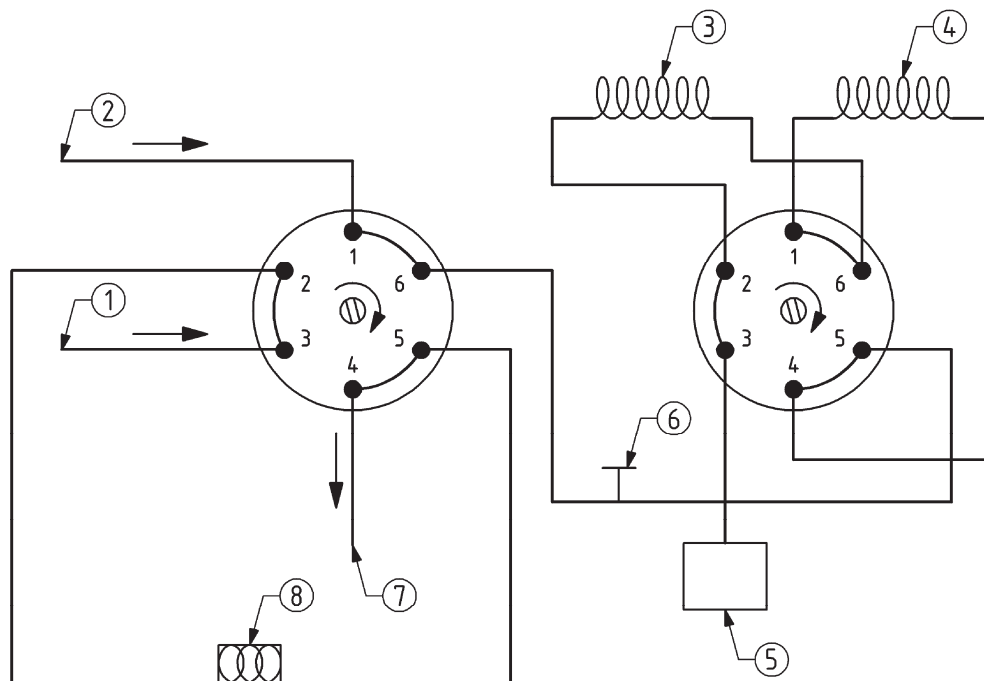
**Figure A.4 — Valve configuration for the sampling and elution of He and H<sub>2</sub>**



**Key**

- |   |                |    |              |
|---|----------------|----|--------------|
| 1 | carrier        | 7  | carrier      |
| 2 | gas sample out | 8  | column 4     |
| 3 | gas sample in  | 9  | needle valve |
| 4 | sample loop    | 10 | TCD          |
| 5 | column 3       | 11 | column 6     |
| 6 | vent He        |    |              |

**Figure A.5 — Valve configuration for the sampling and elution of CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, N<sub>2</sub>, CO and CH<sub>4</sub>**



**Key**

- |   |               |   |                  |
|---|---------------|---|------------------|
| 1 | gas sample in | 5 | FID              |
| 2 | carrier       | 6 | Split/ Splitless |
| 3 | column 2      | 7 | gas sample out   |
| 4 | column 1      | 8 | sample loop      |

**Figure A.6 — Valve configuration for the sampling and elution of the hydrocarbons**

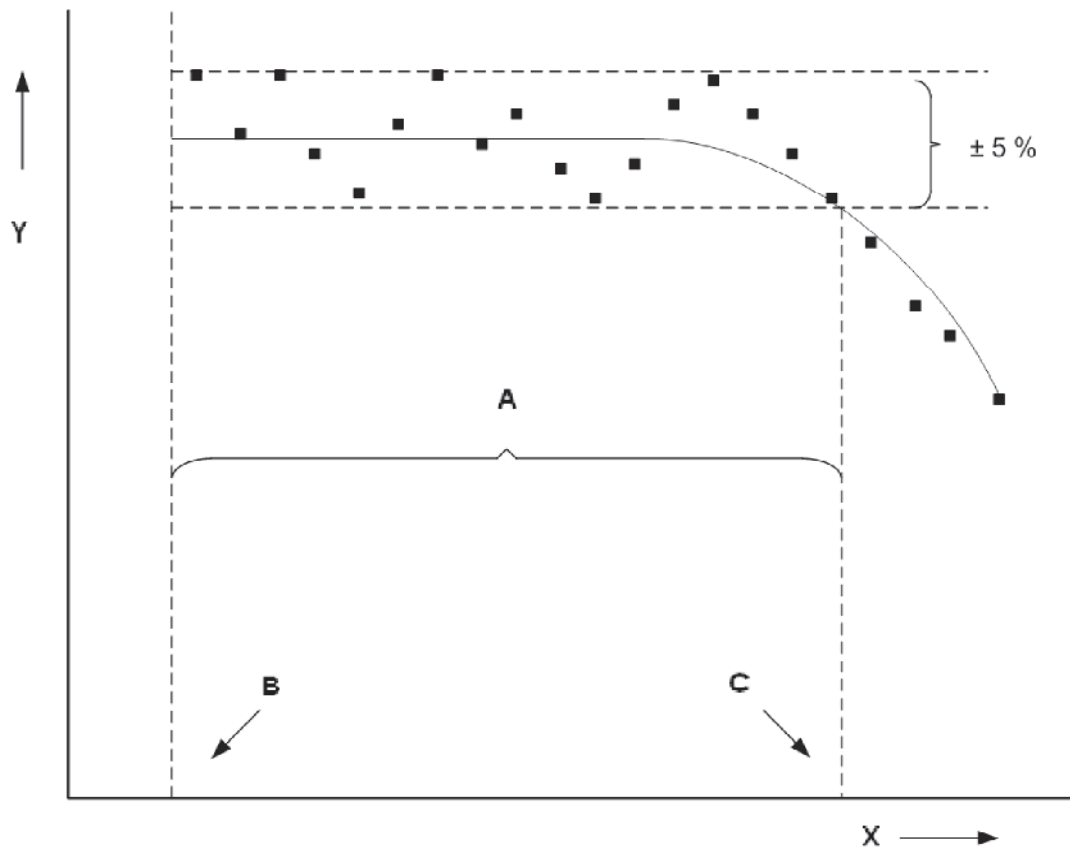
## Annex B (normative)

### Detector linearity check

The linear range of a chromatographic detector represents the range of concentrations or mass flows of a substance in the mobile phase at the detector over which the sensitivity of the detector is constant within a specified variation, usually  $\pm 5\%$  relative.

NOTE The linearity check is derived from DIN 51405 [2].

The best way to present detector linear range is the linearity plot (see Figure B.1) plotting detector sensitivity against amount injected, concentration or mass flow-rate. Here, the upper limit of linearity can be graphically established as the amount (concentration, or mass flow-rate) at which the deviation exceeds the specified value. The lower limit of linearity is always the minimum detectable amount determined separately for the same compound.



#### Key

A linear range

B minimum detectability

C upper limit linear range

X concentration or mass flow

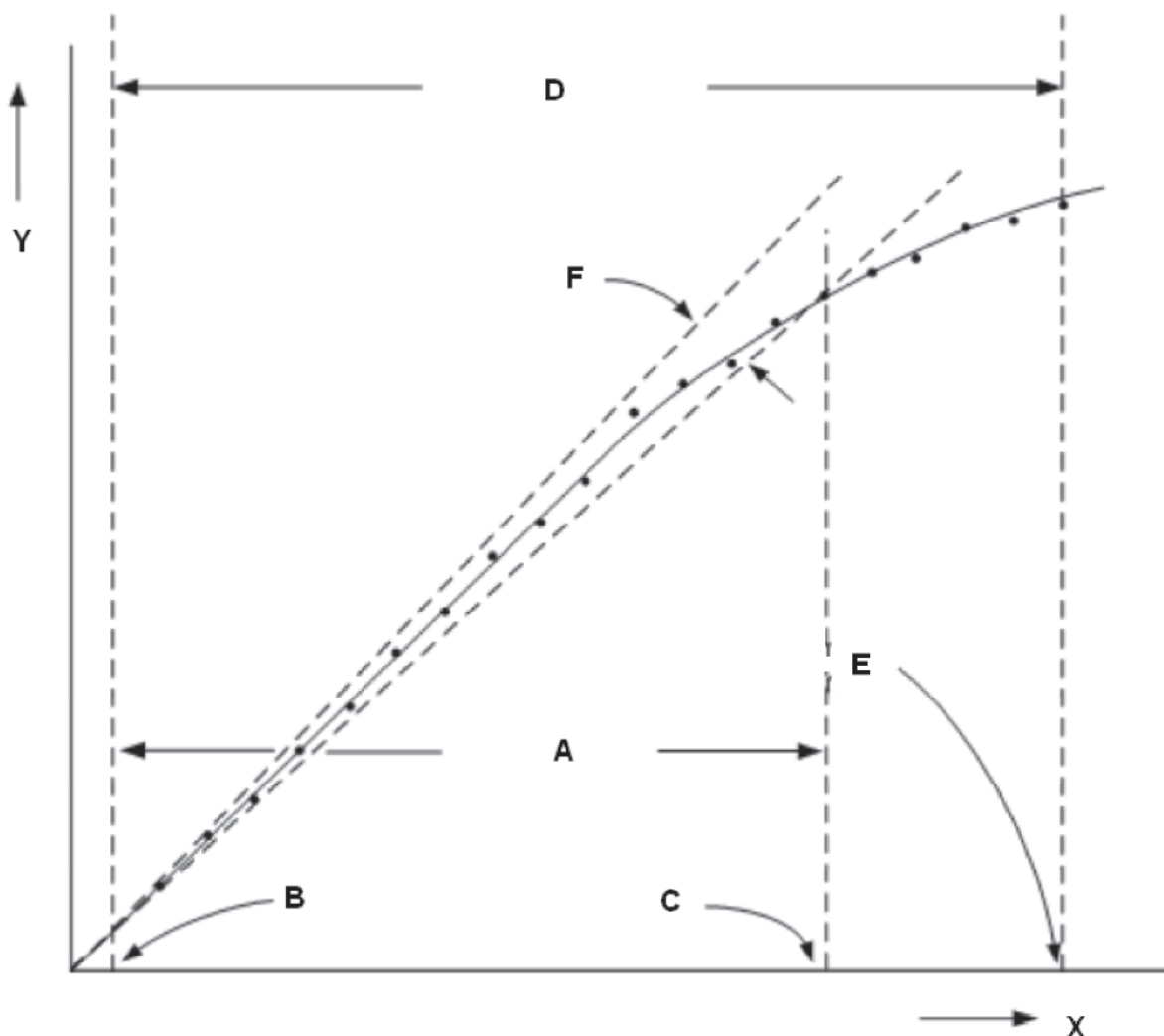
Y detector sensitivity

Figure B.1 — Linearity plot

Alternatively, the linear range of a detector may be presented as the plot of peak area (height) against concentration or mass flow-rate of the test substance in the column effluent at the detector (see Figure B.2). This plot may be either linear or log/log. The upper limit of linearity is that concentration (or mass flow-rate) at which the deviation from an ideal linearity plot is greater than the specified percentage ( $\pm 5\%$ ).

Numerically, the linear range may be expressed as the ratio of the upper limit of linearity obtained from the linearity plot and the minimum detectability, both measured for the same substance.

When presenting the linear range of a detector, either as a plot or as a numerical value, the test substance, the minimum detectability, and the specified deviation shall be stated.



**Key**

- |   |                          |   |                              |
|---|--------------------------|---|------------------------------|
| A | linear range             | E | upper limit of dynamic range |
| B | minimum detectability    | F | 5% window                    |
| C | upper limit of linearity | X | concentration or mass flow   |
| D | dynamic range            | Y | detector signal (peak area)  |

**Figure B.2 — Alternative linear range representation**

## Annex C (informative)

### Calculation test data

This Annex may be used to verify the calculation procedures for determining the carbon content and calorific value of a gas mixture. Two sets of compositions (S1 & S2) are given in Table C.1 with their corresponding results when performing the calculations according to Clause 7 and using the component data from Table D.1.

By entering the compositional data for S1 or S2 into the actual calculation program in use, the calculation procedure can be verified by comparing these results to the values given in Table C.1.

**Table C.1 — Test data for verifying carbon content and calorific value calculations**

Component	Composition		Carbon Content		Calorific Value	
	mol/100 mol	mol/100 mol	g C/100 g	g C/100 g	kJ/100 g	kJ/100 g
	S1	S2	S1	S2	S1	S2
Hydrogen	50,00	10,00	0,00	0,00	650,20	73,04
Argon	2,50	1,00	0,00	0,00	0,00	0,00
Nitrogen	10,00	43,00	0,00	0,00	0,00	0,00
Carbon monoxide	3,00	1,00	1,94	0,36	45,66	8,55
Carbon dioxide	1,00	3,00	0,65	1,09	0,00	0,00
Methane	10,00	5,00	6,46	1,81	431,79	121,26
Ethane	3,00	4,00	3,88	2,90	230,61	172,70
Ethylene	2,00	2,00	2,58	1,45	142,38	79,97
Acetylene	0,50	1,00	0,65	0,73	33,81	37,98
Propane	4,00	6,00	7,75	6,53	439,72	370,46
Propylene	2,00	3,00	3,88	3,27	207,23	174,59
Propyne	1,00	0,00	1,94	0,00	99,79	0,00
Propadiene	0,50	1,00	0,97	1,09	49,90	56,05
<i>iso</i> -butane	3,50	5,00	9,05	7,26	498,71	400,15
<i>n</i> -Butane	1,00	3,00	2,58	4,36	142,96	240,88
<i>trans</i> -2-Butene	0,00	3,00	0,00	4,36	0,00	229,38
1-Butene	1,00	2,00	2,58	2,90	136,70	153,56
<i>iso</i> -Butylene	1,00	1,00	2,58	1,45	135,80	76,27
<i>cis</i> -2-Butene	0,00	1,00	0,00	1,45	0,00	76,58
1,3-Butadiene	3,00	3,00	7,75	4,36	388,74	218,34
<i>iso</i> -pentane	0,60	0,75	1,94	1,36	105,38	73,98
<i>n</i> -Pentane	0,30	0,75	0,97	1,36	52,81	74,15
C6+ backflush	0,10	0,50	0,39	1,09	20,91	58,73
<b>Total:</b>	<b>100,00</b>	<b>100,00</b>	<b>58,54</b>	<b>49,18</b>	<b>3813,11</b>	<b>2696,61</b>

## Annex D (normative)

### Data for calculation

The carbon content, molar heating value and calorific value at 15° C that shall be used for the calculations are given in Table D.1.

**Table D.1 —Component data for carbon content and calorific value**

No	Component	Formula	Molar mass $M_i$ (g/mol)	Carbon content $W_{C_i}$ (gC/g)	Molar heating value $H_{u_i}$ (kJ/mol)	Calorific value (mass based) $H_{u_{C_i}}$ (kJ/g)
1	Hydrogen	H <sub>2</sub>	2,015 9	0	241,72	119,91
2	Helium	He	4,002 6	0	0	0
3	Oxygen	O <sub>2</sub>	31,998 8	0	0	0
4	Argon	Ar	39,948	0	0	0
5	Nitrogen	N <sub>2</sub>	28,013 5	0	0	0
6	Carbon monoxide	CO	28,010	0,428 8	282,91	10,10
7	Carbon dioxide	CO <sub>2</sub>	44,010	0,272 9	0	0
8	Hydrogen sulfide	H <sub>2</sub> S	34,082	0	517,95	15,20
9	Carbon	C	12,011	1,000 0		
10	Methane	CH <sub>4</sub>	16,043	0,748 7	802,69	50,03
11	Ethane	C <sub>2</sub> H <sub>6</sub>	30,070	0,798 9	1 428,84	47,52
12	Ethene	C <sub>2</sub> H <sub>4</sub>	28,054	0,856 3	1 323,24	47,17
13	Ethyne (Acetylene)	C <sub>2</sub> H <sub>2</sub>	26,038	0,922 6	1 256,94	48,27
14	Propane	C <sub>3</sub> H <sub>8</sub>	44,097	0,817 1	2 043,37	46,34
15	Propene	C <sub>3</sub> H <sub>6</sub>	42,081	0,856 3	1 926,13	45,77
16	Propyne (Methylacetylene)	C <sub>3</sub> H <sub>4</sub>	40,065	0,899 4	1 855,09	46,30
17	Propadiene	C <sub>3</sub> H <sub>4</sub>	40,065	0,899 4	1 855,09	46,30
18	<i>iso</i> -Butane	C <sub>4</sub> H <sub>10</sub>	58,123	0,826 6	2 648,42	45,57
19	<i>n</i> -Butane	C <sub>4</sub> H <sub>10</sub>	58,123	0,826 6	2 657,60	45,72
20	<i>trans</i> -2-Butene	C <sub>4</sub> H <sub>8</sub>	56,108	0,856 3	2 530,50	45,10
21	1-Butene	C <sub>4</sub> H <sub>8</sub>	56,108	0,856 3	2 540,97	45,29
22	2-Methyl-Propene	C <sub>4</sub> H <sub>8</sub>	56,108	0,856 3	2 524,30	44,99
23	<i>cis</i> -2-Butene	C <sub>4</sub> H <sub>8</sub>	56,108	0,856 3	2 534,20	45,17
24	1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	54,092	0,888 2	2 408,80	44,53
25	<i>iso</i> -Pentane	C <sub>5</sub> H <sub>12</sub>	72,150	0,832 4	3 265,08	45,25
26	<i>n</i> -Pentane	C <sub>5</sub> H <sub>12</sub>	72,150	0,832 4	3 272,00	45,35
27	Other components with 5 or more carbon atoms	(C <sub>6</sub> H <sub>14</sub> )	86,177	0,836 3	3 887,21	45,11

## Bibliography

- [1] EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259:2006)*
- [2] DIN 51405, *Testing of mineral oil hydrocarbons, similar liquids and solvents for paints and varnishes — Analysis by gas chromatography — General working principles*
- [3] DIN 51666, *Testing of petroleum products — Determination of composition for calculation of carbon content and calorific value of heating gas from refineries — Gas chromatography method*







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