![SIST logo]

SLOVENSKI STANDARD
oSIST prEN 15984:2021

01-maj-2021

Naftna industrija in proizvodi - Določevanje sestave rafinerijskega plina za ogrevanje in izračunavanje vsebnosti ogljika in kalorične vrednosti - Plinska kromatografska metoda

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

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

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

Ta slovenski standard je istoveten z: prEN 15984

ICS:

71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.160.30	Plinska goriva	Gaseous fuels

oSIST prEN 15984:2021   **en**

iTeh STANDARD PREVIEW
(standards.iteh.ai)

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 15984

May 2021

ICS 75.160.30

Will supersede EN 15984:2017

English Version

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 draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 19.

iTeh STANDARD PREVIEW

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Ref. No. prEN 15984:2021 E

prEN 15984:2021 (E)

Contents

Page

European foreword

This document (prEN 15984:2021) 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 document is currently submitted to the CEN Enquiry.

This document will supersede EN 15984:2017.

This revision contains a new informative Annex with estimated precision data for selected components in refinery gas.

This document has been is based on a DIN Standard [5] with the same scope.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

1   Scope

This document 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 document, the terms "% (V/V)" is used to represent the volume fraction (φ).

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

2   Normative references

There are no normative references in this document.

3   Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

4   Principle

This document 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 results in the precision as described in Clause 11.

Table 1 — Refinery heating gas components

Number	Description	Chemical formula
1	Hydrogen	H_2
2	Oxygen/Argon	O_2/Ar
3	Nitrogen	N_2
4	Carbon monoxide	CO
5	Carbon dioxide	CO_2
6	Hydrogen sulfide	H_2S
7	Methane	CH_4
8	Ethane	C_2H_6
9	Ethene	C_2H_4
10	Ethyne (Acetylene)	C_2H_2
11	Propane	C_3H_8
12	Propene	C_3H_6
13	Propyne (Methylacetylene)	C_3H_4
14	Propadiene	C_3H_4
15	*iso*-Butane	C_4H_{10}
16	*n*-Butane	C_4H_{10}
17	*trans*-2-Butene	C_4H_8
18	1-Butene	C_4H_8
19	2-Methyl-Propene	C_4H_8
20	*cis*-2-Butene	C_4H_8
21	1,3-Butadiene	C_4H_6
22	*iso*-Pentane	C_5H_{12}
23	*n*-Pentane	C_5H_{12}
24	Other components with 5 or more Carbon atoms, excluding *iso*- and *n*-Pentane (C_{5+})	

5   Reagents and materials

5.1 Gases.

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

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

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

5.1.4   Air, free of oil and water.

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

5.2 Calibration sample.

A certified reference gas mixture in concentrations that allow the determination of the necessary response factors (see 8.1) and retention times is required.

6   Apparatus

6.1   Usual laboratory apparatus and glassware.

6.2   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 7.

7   Gas chromatographic analysis

7.1 Analysis systems

The gas chromatographic system, as recommended in Annex A, 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© and Molsieve© are examples of such commercially available columns[1].

   Hydrogen is determined on a TCD with nitrogen (5.1.3) 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 (5.1.2) 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_2/Ar, N_2, CH_4 and CO) are on the molecular sieve 13X column, this column is isolated. Carbon dioxide, the C_2-hydrocarbons and hydrogen sulfide are eluted from the porous polymer column (column 4) and are detected. The C_2-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.

---

[1] HayeSep© and Molsieve© are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of these products.

3) Analysis system 3

The third analysis system separates and quantifies all hydrocarbons by an FID and hydrogen (5.1.1) or helium (5.1.2) 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.

7.2 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.

Optionally a vaporizer may be used.

7.3 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_{5+} 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.

8 Calibration

8.1 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 7.1) 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 shall be used (see 8.3).

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

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

8.2 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 as follows:

$$RF_i = \frac{x_i}{A_i}$$

(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.

8.3 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 as follows:

$$RRF_i = \frac{RF_i}{RF_{St}}$$

(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.

9 Calculation

9.1 General

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

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

9.2 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 Formula (3):

$$x_{i,sample} = A_{i,sample} \times RRF_{i,St} \times RF_{StK}$$ (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 Formula (3) RRF = 1 and each RF represents the individual component i.

9.3 Validation of normalized composition (reference components)

The results may 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:

$$x_i^* = \frac{x_{i,sample}}{\sum\limits_{i=1}^{k} x_{i,sample}} * 100$$ (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;

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

k is the number of components.

9.4 Calculation of carbon content

The determined and normalized concentrations of each component, calculated according to Formulae (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: