International Standard



INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•ME#ДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Natural gas – Determination of hydrogen, inert gases and hydrocarbons up to C_8 – Gas chromatographic method

Gaz naturel — Détermination de l'hydrogène, des gaz inertes et des hydrocarbures jusqu'en C_8 — Méthode par chromatographie en phase gazeuse

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Descriptors : natural gas, gas analysis, determination of content, hydrogen, helium, hydrocarbons, gas phase chromatography, quantitative analysis, apparatus.

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6974 was prepared by Technical Committee ISO/TC 158, Analysis of gases. (standards.iteh.ai)

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Natural gas – Determination of hydrogen, inert gases and hydrocarbons up to C_8 – Gas chromatographic method

0 Introduction

This International Standard describes a precise and accurate method for the analysis of natural gas.

The method requires the use of two columns which can be put into one or two gas chromatographs. The constituents of the eluent of the first column are detected by a thermal conductivity detector (TCD). The constituents of the eluent of the second column are detected by a TCD and flame ionization detector (FID) in series.

NOTE – If the two columns are put in one chromatograph the procedure given in clause A.6 should be followed.

simple method for the analysis up to C5 of constituents of dry

natural gas by gas chromatography, or to ISO 6569, which describes a rapid evaluation up to C_4 of constituents of natural

For analysis of natural gas for hydrocarbons from butane (C_4)

This International Standard specifies a method of quantitative

The detectors and associated electronics shall have a rapid ISO 6143, *Gas analysis – Determination of composition of response time – a time constant of not greater than 0,1 s is calibration gas mixtures – Comparison methods.* desired.

ISO 6146, Gas analysis – Preparation of calibration gas mix-The method allows measurement of helium, hydrogen<u> $_{0}$ (0xy)74:198tures</u> – Manometric method. gen, nitrogen, carbon dioxide and C₁ up to C₈ hydrocarbons hard/site/48c631-920a-4c0b-b192-

If the content of hydrocarbons only up to C_4 or C_5 is required, iso-69 tography. reference can be made either to ISO 6568, which describes a

ISO 6569, Natural gas — Rapid analysis by gas chromatography.

ISO 6975, Natural gas — Determination of hydrocarbons from butane (C₄) up to hexadecane (C₁₆) — Gas chromatographic method.²⁾

3 Principle

Separation of the components of natural gas by means of two chromatographic columns. Use of a molecular sieve 13 X³ column with a TCD for the separation and detection of helium, hydrogen, oxygen and nitrogen, and a Porapak R³ column with a TCD and an FID in series for the separation and detection of nitrogen, carbon dioxide and hydrocarbons from C₁ up to C₈. The two analyses are carried out independently and the results are combined.

If oxygen is seen to be present at a concentration greater than 0,02 % (mol/mol) when measuring on molecular sieve, then

gas by gas chromatography.

helium

hydrogen

oxygen

nitrogen

1

up to hexadecane (C₁₆), see ISO 6975.

Scope and field of application

analysis of the following constituents of natural gas

- carbon dioxide
- hydrocarbons from C_1 up to C_8

The gas sample shall not contain any hydrocarbon condensate and/or water.

2 References

ISO 683/13, Heat-treated steels, alloy steels and free-cutting steels – Part 13 : Wrought stainless steels.¹⁾

ISO 6142, Gas analysis – Preparation of calibration gas mixtures – Weighing methods.

¹⁾ At present at the stage of draft. (Revision of ISO 683/13-1974.)

²⁾ At present at the stage of draft.

^{3) 13} X and Porapak R are trade names for commercially available products. At present, no other products intended for this purpose are known to be available commercially. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of these products by ISO.

the nitrogen value shall be taken from the molecular sieve analysis. If less than 0,02 % (mol/mol) of oxygen is present, the nitrogen value is taken from the Porapak R analysis. Quantitative results are achieved by calibration of the detectors with calibration gas mixtures. The response factors of helium, hydrogen, oxygen, nitrogen, carbon dioxide and the saturated hydrocarbons from methane up to butane are derived from an analysis of calibration gas mixtures. The relative response factors to butane of isobutane and higher hydrocarbons are given in table 5.

The resulting composition of the natural gas is normalized to 100 % (see 8.1).

4 Materials

4.1 Materials for the determination of helium, hydrogen, oxygen and nitrogen

4.1.1 Carrier gas – argon, \ge 99,99 % pure¹), free from oxygen and water.

4.1.2 Reference materials.

4.1.2.1 Helium, oxygen and hydrogen 99% pure. DA NOTE _ A more accurate flow controller may be used.

4.1.2.2 Nitrogen and methane, > 99,99 % putel, free ards, 12 injection device, bypass-type injector (gas sampling from helium, oxygen and hydrogen. valve), capable of injecting a volume of 1 ml.

ISO 6974:1984

4.2 Materials for the determination of nitrogen discussion discussin discussin discussion discussion discussion discussion discuss

4.2.1 Carrier gas – helium, \geq 99,99 % pure¹⁾, free from oxygen and water.

4.2.2 Auxiliary gases.

4.2.2.1 Hydrogen, 99,99 % pure¹), free from corrosive gases, water and organic compounds.

4.2.2.2 Air, free from hydrocarbon impurities.

4.2.3 Reference materials.

4.2.3.1 Nitrogen and methane, > 99,99 % pure.

4.2.3.2 Carbon dioxide, ethane, propane and butane, > 99,95 % pure¹⁾.

Other reference materials which may be used for peak identification are pentane, hexane, heptane, octane, benzene, toluene, cyclohexane, isobutane, 2-methylbutane, neopentane and methylcyclohexane.

5 Apparatus

5.1 Apparatus for the determination of helium, hydrogen, oxygen and nitrogen

5.1.1 Gas chromatograph, capable of temperature programmed operation and equipped with a TCD.

5.1.1.1 Column oven and temperature control

5.1.1.1.1 Column oven, temperature range 35 to 350 °C, capable of being maintained to within \pm 0,5 °C at any temperature in the range during an analysis. To obtain a temperature of 35 °C an accessory for cooling with liquid carbon dioxide or liquid nitrogen may be necessary.

NOTE – Alternative procedures for analysis on the molecular sieve 13 X column are given in clause A.4.

5.1.1.1.2 Temperature control: The oven shall be provided with a linear programmer suitable for providing a rate of temperature increase of 30 °C/min over the specified range.

5.1.1.2 Flow regulators, to give suitable carrier gas flow rates.

iso-6974-1984 Two columns with the same type of packing and with the same dimensions (see 7.1.1.1.2).

NOTE — The second column is normally used for drift compensation during a temperature programme. If drift compensation is done by means of the electronic integrator a second column is not necessary.

5.1.3.1 Tube

 Nature : stainless steel, number 20 according to ISO 683/13 (AISI type 316), cleaned and degreased

- Length: 1 m
- Diameter : 2 mm internal diameter
- Form : appropriate to the chromatograph
- Radius : appropriate to the chromatograph

5.1.3.2 Packing

5.1.3.2.1 Molecular sieve 13 X

Particle size : 150 to 180 µm (80 to 100 ASTM mesh)

¹⁾ If the purity of the gas is less than that specified, it is essential to check that the type of impurity present does not interfere with the analysis. Also, even if the carrier gases argon and/or helium fall within the specification, some of the impurities present in these gases can nevertheless interfere with the analysis. Under these circumstances, appropriate purification is essential.

After packing, treatment overnight at approximately 350 $^{\rm o}{\rm C}$ with carefully dried carrier gas flowing is necessary for good separation.

5.1.3.2.2 Method of packing

Any method which results in uniform column packing may be used.

NOTE – The following method is suitable.

The column outlet is closed with a sintered disc or glass-wool plug. A reservoir containing rather more packing than is needed to fill the column is connected to the inlet and a pressure of 0,4 MPa of nitrogen is applied to this reservoir. The flow of packing into the column is assisted by vibration. When the column is full, allow the pressure to decay slowly before disconnecting the reservoir.

5.1.3.2.3 Efficiency of resolution

Inject a sample containing equivalent amounts (in the region of 0,4 %) of hydrogen and helium so that the height of the valley between the peaks above the baseline is not greater than 10 % of the height of the larger peak under the operation conditions stated in 7.1. If this criterion is not met continue the activation for a longer period or prepare a new column.

temperature of 35 °C an accessory for cooling with liquid carbon dioxide or liquid nitrogen may be necessary.

5.2.1.1.2 Temperature control : the oven shall be provided with a linear programmer suitable for providing a rate of temperature change of 15 $^{\circ}$ C/min over the specified range.

5.2.1.2 Flow regulators, to give suitable carrier gas flow rates.

NOTE - A more accurate flow controller may be used.

5.2.2 Injection device, bypass-type injector (gas sampling valve), with heating device, capable of injecting a volume of 0,5 ml.

5.2.3 Columns

Two columns with the same type of packing and with the same dimensions (see 7.2.1.1.2).

NOTE – The second column is normally used for drift compensation during a temperature programme. If drift compensation is done by means of the electronic integrator a second column is not necessary.

5.1.4 Thermal conductivity detector, with a time constant RD5.2.3.R Fube IEW of not greater than 0,1 s.

5.1.5 Potentiometric recorder

(standards.iteh.Nature : stainless steel, number 20 according to ISO 683/13 (AISI type 316), cleaned and degreased

- Range : appropriatent of the detector averally standards/sist/c4f8c631-920a-4c0b-b192-10 mV) 136253c06632/iso-6974-1984Diameter : 2 mm internal diameter

- Impedance : > 2 000 Ω
- Response time : \leq 0,5 s

NOTE – Alternative devices may be used provided that the requirements for response are satisfied.

5.1.6 Integrator

Wide range : 0 to 1 V

The integrator shall be capable of baseline tracking and of measuring peaks on a sloping baseline.

5.2 Apparatus for the determination of nitrogen, carbon dioxide and hydrocarbons from C_1 up to C_8

5.2.1 Gas chromatograph, for the analysis of gases suitable for dual column application equipped with a TCD and an FID in series. The FID shall have a linear dynamic range of six decades and a lower limit of detection of 10^{-12} g/s of carbon.

5.2.1.1 Column oven and temperature control

5.2.1.1.1 Column oven, temperature range 35 to 300 °C, capable of being maintained to within \pm 0,5 °C at any temperature in the range during an analysis. To obtain a

- Form : appropriate to the chromatograph
- Radius : appropriate to the chromatograph

5.2.3.2 Packing

5.2.3.2.1 Porapak R

Particle size : 150 to 180 µm (80 to 100 ASTM mesh)

After packing, treatment overnight at approximately 230 °C with carefully dried carrier gas flowing is necessary for good separation.

5.2.3.2.2 Method of packing

Any method which results in uniform column packing may be used. A suitable method is described in the note to 5.1.3.2.2.

5.2.3.2.3 Efficiency of resolution

Inject a natural gas sample so that the height of the valley between the 2-methylbutane and pentane peaks above the baseline is not greater than 10 % of the height of the larger peak under the operation conditions stated in 7.2. If this criterion is not met continue the activation for a longer period or prepare a new column.

5.2.4 Detectors

For components including hydrocarbons up to C₃: TCD

For hydrocarbons from C₄ up to C₈ : FID

Ethane and propane can be detected by an FID if the concentration is less than 1 %.

In either case the time constant shall not be greater than 0,1 s. The TCD and FID detectors shall be connected in series.

5.2.5 Potentiometric recorder(s)

In the case of non-automatic change-over from TCD to FID, a dual pen recorder is necessary to detect both signals in parallel.

In the case of automatic change-over from TCD to FID, a single pen recorder is sufficient.

- Range : appropriate to detector (usually 1 to 10 mV)
- Response time : $\leq 0,5$ s

7 Procedure

If the apparatus has been used for a previous determination ensure that it has returned to the starting conditions in 7.1.1 before injecting a sample or calibration gas mixture.

Inject the sample into two columns according to 7.1 and 7.2.

Modifications of the procedure that are not part of the standard are described in annex A.

7.1 Determination of helium, hydrogen, oxygen and nitrogen

7.1.1 Control of the apparatus

Set up the gas chromatograph according to the manufacturer's instructions.

Set the heater of the bypass injector to 50 °C.

7.1.1.1 Oven and column

7.1.1.1.1 Temperature programme :

iTeh STANDARaD initial temperature 35 °C for 7 min; NOTE – Alternative devices may be used provided that the requirements for response are satisfied.

5.2.6 Integrator

Wide range : 0 to 1 V

ISO 6974:1984 maintain at 250 °C for 10 min.

https://standards.iteh.ai/catalog/standards/cist/c486631.920a-4c0h-h192-analysis on the molecular sieve 136253c06632/column/arel given in clause A.4.

The integrator shall be capable of baseline tracking and of measuring peaks on a sloping baseline.

Samples 6

The method is intended for natural gases containing constituents in the ranges listed in table 1. They do not represent the limit of detection, but the limits within which the stated precision of the method applies. If one or more components in a sample is not detectably present, the method can still be used.

Table 1 – Concentration ranges of natural gas components

Component	Range [% (mol/mol)]
Helium	0,01 to 0,5
Hydrogen	0,01 to 0,5
Oxygen	0,1 to 0,5
Nitrogen	0,1 to 40
Carbon dioxide	0,1 to 30
Methane	50 to 100
Ethane	0,1 to 15
Propane	0,001 to 5
C ₄ hydrocarbons up to octane	0,001 to 0,5

7.1.1.1.2 Carrier gas flow rate

10 ml of argon per minute

7.1.1.2 Detector

Detector temperature setting : between 140 and 160 °C.

Set the detector parameters to the maximum setting allowed by the manufacturer at the conditions given above.

7.1.1.3 Recorder

Set the chart speed to a minimum of 0,5 cm/min.

7.1.1.4 Integrator

Set up the integrator in accordance with the manufacturer's instructions. Attenuate the recorder signal, if desired, independently of the integrator input signal.

7.1.2 Calibration

7.1.2.1 At the beginning of each period of use, after the initial sample injection described in 7.1.3, inject the calibration gas mixture (7.1.2.2) twice. The repeatability shall fall within the

relative values quoted in 8.2.1, given the composition of the calibration gas mixture. If this is not achieved, inject the calibration gas mixture a third time, and check the repeatability of the second and third injection. When two successive injections fulfil the repeatability requirement, take the mean of the two as the calibration value.

Recalibration shall be performed at intervals of not greater than 4 h.

NOTE – If more than three replicates are necessary this implies that there may be errors in the procedure or faults in the apparatus.

7.1.2.2 Use gravimetric high pressure calibration gas mixtures (table 2) prepared according to ISO 6142.

 $\mathsf{NOTE}-\mathsf{For}$ alternative methods for the preparation of calibration gas mixtures, see clause A.5.

Component	Gas mixture 1 % (mol/mol)	Gas mixture 2 % (mol/mol)
Helium Oxygen	0,4 0,4	0,4
Hydrogen Nitrogen ¹⁾ Methane ²⁾	iTeh S	0,4 STANDA balance

Table 2 — Calibration gas mixtures

Table 3 - Order of elution of components

Component	Relative retention times
Helium	0,17
Hydrogen	0,21
Oxygen	0,38
Nitrogen	0,69
Methane	1,00
Ethane	3,07

Measure the areas of the peaks due to components in the sample and in the calibration gas mixture. Where a component has been measured at different attenuations in sample and calibration gas mixture, convert the measurements to the same attenuation.

7.1.5 Preliminary expression of results

Calculate the concentration of each component of the sample according to the equation

$$X_{i} = X_{i,c} \left(\frac{A_{i}}{A_{i,c}} \right)$$

$$(1)$$

2) In preparing calibration gas mixtures containing oxygen and methane, it is essential that the proportions of oxygen and methane lierds/sist/c41X2631is)the mole fraction, expressed as a percentage, of outside the explosive limits. 136253c06632/iso-6974_substance *i* in the calibration gas mixture;

7.1.3 Test

Purge the sample valve with the gas to be analysed, using at least 20 times the volume of the valve and associated pipework.

Stop the purge so as to allow the gas to reach the temperature of the valve and ambient pressure, then inject.

Inject the appropriate calibration gas mixture in the same way.

If this volume of sample is not enough to purge the valve, contamination by air or by the previous sample will be evident. In this case, use a larger volume of sample for purging.

NOTE - It is also possible to introduce the sample into a previously evacuated sample loop and allow it to equilibrate to ambient pressure before injection.

7.1.4 Examination of the chromatogram

A typical chromatogram is shown in figure 1.

The order of elution of components and information on relative retention times for a properly prepared column are given in table 3. Table 3 has to be used with care because relative retention times are unreliable on a molecular sieve column as they depend upon the conditions of preparation and state of use of the column. The column can be regenerated by overnight heating at 350 °C (see 5.1.3.2.1).

 A_i is the area of the peak for substance *i* on the chromatogram of the sample;

 $A_{i,c}$ is the area of the peak for substance *i* on the chromatogram of the calibration gas mixture.

7.2 Determination of nitrogen, carbon dioxide and hydrocarbons from C_1 up to C_8

7.2.1 Control of the apparatus

Set up the gas chromatograph according to the manufacturer's instructions.

Set the heater of the bypass injector to 100 °C.

7.2.1.1 Oven and column

7.2.1.1.1 Temperature programme :

- a) initial temperature 35 °C for 3 min;
- b) heat at 15 °C/min to 200 °C;
- c) maintain at 200 °C for 30 min.

7.2.1.1.2 Carrier gas flow rate

35 ml of helium per minute

7.2.1.2 Detectors

TCD temperature setting : between 240 and 260 °C

Set the bridge current according to manufacturer's intructions.

FID temperature setting : between 290 and 310 °C

Adjust the hydrogen and air flow rates so as to give optimum response as recommended by the manufacturer. Light the flame in the FID.

7.2.1.3 Recorder(s)

Set the chart speed to a minimum of 0,5 cm/min.

7.2.1.4 Integrator(s)

Set up the integrator(s) in accordance with the manufacturer's instructions. Attenuate the recorder signal independently of the integrator input signal.

ISO 69columns have been installed.

7.2.2 Calibration

7.2.2.1 At the beginning of each period of use, after the initial sample injection described in 7.1.3, inject the calibration gas mixture (7.2.2.2) twice. The repeatability shall fall within the relative values quoted in 8.2.1, given knowledge of the composition of the calibration gas mixture. If this is not achieved, inject the calibration gas mixture a third time, and check the repeatability of the second and third injection. When two successive injections fulfil the repeatability requirement, take the mean of the two as the calibration value.

Recalibration shall be performed at intervals of not greater than 4 h.

NOTE - If more than three replicates are necessary this implies that there may be errors in the procedure or faults in the apparatus.

7.2.2.2 Use gravimetric high pressure calibration gas mixtures prepared according to ISO 6142.

The mixture should contain nitrogen, carbon dioxide, methane, ethane, propane and butane.

In order to obtain maximum accuracy, the tolerances between the concentration of the indicated components of the calibration gas mixture and the components of the sample shall be as given in table 4.

Sample actual component concentration	Calibration gas mixture deviation of component concentration
% (mol/mol)	% relative to sample concentration
0,001 to 0,1 0,1 to 1 1 to 10 10 to 50 50 to 100	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

7.2.3 Test

Proceed in a similar way to that described in 7.1.3.

7.2.4 Examination of the chromatogram

A typical chromatogram is shown in figure 2.

NOTES

1 Different batches of Porapak R often show slight variation in periTeh STAND formance. For example the retention sequence of benzene and cyclohexane may be reversed.

> It is therefore recommended that the retention times of benzene and cyclohexane be determined from time to time, and certainly after new

https://standards.iteh.ai/catalog/standards/sist/c4f8c631-920a-4c0b-b192-Baseline_stability may be checked as follows : 136253c06632/iso-69/4-1984

First, raise the oven to the final temperature (7.2.1.1.1) to clear any accumulated contamination.

Second, cool to the initial temperature.

Third, inject a calibration gas mixture containing a low concentration of butane and start the temperature programme (7.2.1.1.1).

Fourth, at the end of the calibration gas run, cool to the initial temperature. Perform a blank run by injecting carrier gas in place of a sample (see 7.1.3) and start the temperature programme.

Fifth, calculate the concentrations of the constituents of which the peaks are recognized by the integrator in the C5 up to C8 region by comparison with the butane in the calibration gas.

No individual peak should originate from a constituent with a concentration exceeding 0,04 % (mol/mol). If larger peaks are seen, repeat blank runs until satisfactory. If necessary, prepare new columns, preferably from a different batch of Porapak R.

Measure the areas of the peaks due to components in the sample and in the calibration gas mixture. Where a component has been measured at different attenuations in sample and calibration gas mixture, convert the measurements to the same attenuation.

7.2.5 Preliminary expression of results

Calculate the concentration of each component of the sample according to equation (1).

To determine the cyclic and acyclic hydrocarbon components with 4 up to 8 carbon atoms (these components are not present in the calibration gas mixture), apply relative response factors of the FID for these components compared to butane, either experimentally determined or those given in table 5.

Calculate the concentration of the cyclic and acyclic hydrocarbon components with 4 up to 8 carbon atoms according to the equation

$$X_i = F_i \left(\frac{A_i}{A_b}\right) X_b \qquad \dots (2)$$

where

 X_i is the mole fraction, expressed as a percentage, of substance i in the sample;

 $X_{\rm b}$ is the mole fraction, expressed as a percentage, of butane in the sample;

 F_i is the response factor of the FID of substance i compared to butane;

 A_i is the area of the peak for substance i on the chromatogram of the sample Teh STANDA b) if the oxygen concentration of the samples is greater than 0,02 % (mol/mol), then the nitrogen concentration of the samples shall be taken from the molecular sieve analysis.

8.1 Normalization

If the sum of the concentrations of all the components, $\sum X_{ii}$

determined in the samples through the molecular sieve and/or Porapak R analysis, adds up to between 99 and 101 %, then the individual concentrations, X_{ii} shall be normalized to 100 % by means of equation (3)

$$X'_{i} = \frac{X_{i}}{\sum_{i=1}^{n} X_{i}} \times 100 \qquad \dots (3)$$

where

ISO 6974:1984

 X'_i is the mole fraction, expressed as a percentage, of substance *i* in the sample after normalization;

 X_i is the mole fraction, expressed as a percentage, of substance i found from either equation (1) or (2); $A_{\rm b}$ is the area of the peak for butane on the chromatogram \sim

en.ai is the total number of components determined separately on both the molecular sieve 13 X and Porapak R

column.
 Table 5 – Relative response factors of the FID for natural
 Countril
 Countril
 gas components

Component	$F_i^{(1)}^{(2)}^{(3)}$
Propane	1,333
Isobutane	1,000
Butane	1,000
Pentanes	0,800
Hexanes	0,667
Heptanes	0,573
Octanes	0,501
Benzene	0,669
Cyclohexane	0,668
Methylcyclohexane	0,572
Toluene	0,572

1) Butane = 1,000

of the sample.

2) These figures are derived from : KAISER, R. Chromatographie in der Gasphase, Part III (1961), p. 136.

The values can only be obtained when using the FID under the 3) conditions of 7.2.1.2.

8 Expression of results

For the final calculations of the concentrations of the components in the samples and for the final presentation of the results, two cases can be distinguished :

a) if less than 0.02 % (mol/mol) of oxygen is present in the samples, then the nitrogen concentration of the samples shall be taken from the Porapak R analysis;

136253c06632/iso-67the concentrations of the components shall be expressed as mole percentages to three significant figures.

> Normally, natural gas does not contain oxygen. If, however, natural gas samples are found to contain oxygen and if this is due to contamination by improper sampling of the gas then the concentration of nitrogen and all the other components shall be corrected according to the following procedure :

a) the sample contains more than 0,02 % (mol/mol) oxygen. If $X_{0_2} > 0.02$ % (mol/mol), correct the nitrogen concentration according to the equation

$$X_{N_{2,c}} = X'_{N_{2}} - \frac{78}{21}X'_{O_{2}}$$
 ... (4)

where

 $X_{N_{2,c}}$ is the mole fraction, expressed as a percentage, of nitrogen after correcting the concentration for air contamination;

 X'_{N_2} is the mole fraction, expressed as a percentage, of nitrogen in the sample after normalization;

 X'_{O_2} is the mole fraction, expressed as a percentage, of oxygen in the sample after normalization.

NOTE - In equation (4) it is assumed that the TCD responses for N_2 and O_2 are equal.