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Draft Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

PART 68 DETERMINATION OF HYDROCARBONS AND NON-HYDROCARBON GASES IN REFINERY GAS STREAMS BY GAS CHROMATOGRAPHY

(ICS 75.080)

Methods for sampling and test for petroleum and related products of natural or synthetic origin (excluding bitumen and hydrogen) Sectional Committee, PCD 01	Last date for receipt of comment is **28 June 2022**

FOREWORD

(*Formal clauses will be added later*)

Refinery gases consist of non-condensable light hydrocarbon gases C_1 to C_6 (traces), non-hydrocarbon gases oxygen, nitrogen, hydrogen, carbon dioxide, carbon monoxide, hydrogen sulphide, acid gases from process units. Also liquefied petroleum gases (LPG) is a major product from the refinery. Toxic gases like hydrogen sulphide and acid gases are to be tested round the clock to ensure smooth and safe refinery operation. Liquefied petroleum gases (LPG) and propylene are being certified in a refinery laboratory regularly. Hydrotreatment and reforming processes in the refinery are generating gas samples to be estimated mainly for hydrogen and hydrocarbon impurities. Refinery furnaces are releasing the flue gases continuously during operation. Uncondensable lighter hydrocarbons, mainly methane and ethane, are used as the gaseous fuel in the refinery furnaces. Decoking operations of the process heaters are also producing gases mainly with oxygen, nitrogen, carbon dioxide, carbon monoxide.

All above stated gases need to be tested for optimum process operation, product certification and compliance to the regulatory norms of air emission from the refinery.

This method is intended to test refinery gases in a single instrument with multicolumn and multidetector configuration of gas chromatograph. Both non-condensable hydrocarbon gases and non-hydrocarbon gases are tested in a single injection to the Refinery Gas Analyser (RGA).

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (*revised*)’.

1 SCOPE

This method is intended for determining quantitative composition of refinery gas streams containing non-condensed hydrocarbon gases with carbon numbers from C_1 to C_{5+} and non-hydrocarbon gases such as H_2, CO_2, O_2, N_2 and CO using a preconfigured multicolumn gas chromatograph. Vaporized liquefied petroleum gas (LPG) is determined for its composition, C_{6+} hydrocarbons are reported as a composite.

1.2 Hydrogen sulphide can be detected with less accuracy due to the loss in sample containers and sample injection tubing, sulphur inert sample containers and sample injection system is required to estimate hydrogen sulphide accurately.

1.3 Non-hydrocarbon gases are estimated in the range 0.03 to 100 mole percent using thermal conductivity detector (TCD) and hydrocarbon gases are estimated in the range 0.005 to 100 mole percent using flame ionization detector (FID).

1.4 This test method is not used to determine individual hydrocarbons greater than C_5, heavier hydrocarbons are reported as C_{6+}.

1.5 Helium and argon in the mixture will interfere with the estimation of hydrogen and oxygen respectively.

1.6 Water vapour will interfere with C_{6+} analysis when TCD is used.

NOTE — This standard does not purport to address all of the safety concerns, if any, 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 prior to use.

2 SUMMARY OF TEST METHOD

The representative sample in gaseous form is injected to the multicolumn gas chromatograph and components are physically separated in the columns. The detector responses are compared to calibration data obtained under identical operating conditions (*see* Annex A) from a reference standard gas mixture of known composition. The heavier hydrocarbons C_{6+} are eluted by backflushing and grouped together to report. The composition of the sample is calculated by comparing the peak areas with the corresponding values obtained with calibration gas mixtures.

3 SIGNIFICANCE AND USE

3.1 The distribution of hydrocarbon components in the gaseous mixture is required for the customers to judge the end use suitability. Trace amount of hydrocarbon impurities and the relative distribution of the components in the mixture are important for using as a feedstock in downstream processing units.

3.2 The component distribution data are used to calculate physical properties of the gas such as relative density, vapour pressure, molecular weight, and heating value.

4 APPARATUS

4.1 Gas Chromatograph

Refinery gas analyzers are available from several suppliers with multicolumn configuration and three detectors to analyze non-condensed hydrocarbons and non-hydrocarbon gases within the scope of this method. Any gas chromatographic instrument with a linear temperature programmable column oven or adequate temperature control to provide the separation of components in the gas sample may be used.

4.1.1 Detector

The type and number of detectors is dependent on the refinery gas analyzer model and the manufacturer. The common refinery gas analyzers (RGA) are having three detector systems:

4.1.1.1 One Flame Ionisation Detector (FID) for the determination of the hydrocarbon gases for the components listed in Table 1.

4.1.1.2 One Thermal Conductivity Detector (TCD) for the determination of hydrogen dedicatedly using nitrogen or argon as the carrier gas.

4.1.1.3 One Thermal Conductivity Detector (TCD) for the determination of all other non-hydrocarbon gases.

4.1.2 A Thermal Conductivity Detector (TCD) may be also used in place of Flame Ionisation Detector (FID) to determine hydrocarbon gases if the concentration is required to determine above 0.03 mole percent.

Table 1 Components to be Determined with FID and TCD

(*Clause* 4.1.1.1)

Sl No.	**Component**	**FID**	**TCD**
(1)	(2)	(3)	(4)
(i)	C_{6+} composite	Yes	Yes
(ii)	Oxygen/Argon		Yes
(iii)	Hydrogen		Yes
(iv)	Carbon dioxide		Yes
(v)	Hydrogen sulphide		Yes
(vi)	Nitrogen		Yes
(vii)	Carbon monoxide		Yes
(viii)	Methane	Yes	Yes
(ix)	Ethane	Yes	Yes
(x)	Ethylene	Yes	Yes
(xi)	Propane	Yes	Yes
(xii)	Propylene	Yes	Yes
(xiii)	Acetylene	Yes	Yes
(xiv)	Isobutane	Yes	Yes
(xv)	Propadiene	Yes	Yes
(xvi)	n-Butane	Yes	Yes
(xvii)	Trans-2-butene	Yes	Yes
(xviii)	1-Butene	Yes	Yes
(xix)	Isobutylene	Yes	Yes
(xx)	Cis-2-butene	Yes	Yes
(xxi)	Neopentane	Yes	Yes
(xxii)	Cyclopentane	Yes	Yes
(xxiii)	Isopentane	Yes	Yes
(xxiv)	Methyl acetylene	Yes	Yes
(xxv)	n-Pentane	Yes	Yes
(xxvi)	1,3-Butadiene	Yes	Yes

4.2 Data Acquisition

Any computerized data acquisition system may be used for display the chromatogram and peak area integration from all the detectors used in the analysis. Normally the Refinery Gas Analyser (RGA) supplier provides the application software to acquire data and to process the data for quantification of the components and tor calibration.

4.3 Sample Introduction

Sample is injected typically with automated valves containing sampling 'loops' of appropriate sizes.

4.4 System Configurations

The Fig. 1 is the typical refinery gas analyser configuration, it may vary among manufacturers. Required sensitivity for the application is achieved by selecting the combination of valve injection size and/or splitting inlet ratio. A typical refinery gas analyser can be summarized from the Fig. 1.

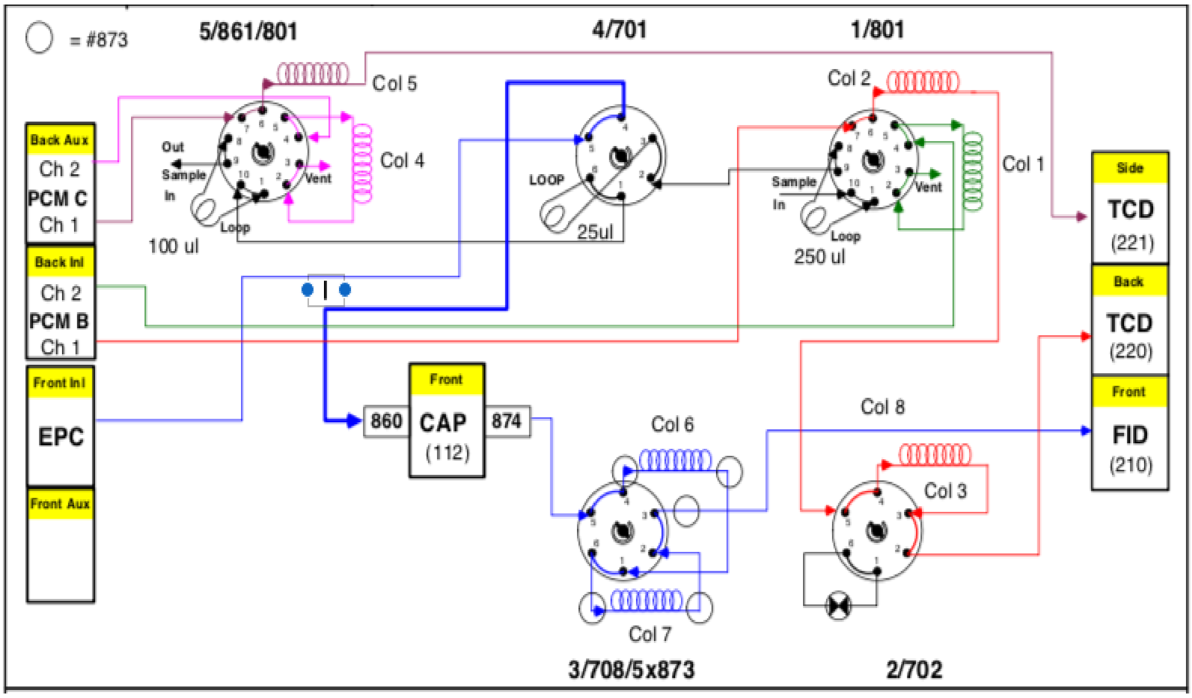

FIG. 1 TYPICAL REFINERY GAS ANALYSER CONFIGURATION

This GC System is configured with five valves and three detectors. The FID channel is configured to analyze the hydrocarbons from C_1 to C_5, while C_6/C_{6+} components are backflushed and measured as one peak at the beginning of the analysis. The first TCD channel (reference gas He) is configured to analyze fixed gases, which may include CO_2, CO, O_2, and N_2. Last, the second TCD channel (third detector, on the side, with reference gas N_2) is dedicated to analyze hydrogen only.

The instrument is configured with capillary inlet (Split/ Split less) and two PCM units acting as flow sources. Both the capillary inlet and the PCM identified as 'B' in the Fig. 1 utilize helium as carrier gas. The last PCM identified as ‘C’ in the diagram, use N_2 as carrier gas in main and secondary intakes. Valves 1, 4 and 5 are gas sampling with sequence reversal and backflush of the pre-column to vent, Valve 2 is a 6 port with column isolation. Valve 3 is a 6 port column sequence reversal with backflush of the pre-column. Last, Valve 4 is a 6 port gas sampling upstream to the capillary inlet.

4.4.1 *Hydrogen Sulphide and Other Reactive Gases*

Samples containing hydrogen sulphide and other reactive gases are required to be handled in inert sample containers such as, sulfinert and also inert sample injection system on the analyser.

4.4.2 *Capillary Columns*

The gas chromatograph must have isothermally operated heated splitting type inlet, or if appropriate, direct connection to the valve may be possible as long as sample sizes are adjusted accordingly, the calibrations are linear and the required resolution of the compounds of interest is maintained. Split ratios are used depending upon the sample injection volume and sensitivity required.

4.4.3 *Pre-concentrator and/or Cryogenic Trapping*

Manufacturer may provide pre-concentrator and/or cryogenic trapping prior to sample introduction into the gas chromatograph to enable to trace level of the component. Manufacturer guideline is to be followed to concentrate any component to analyze accurately.

4.4.4 *Hydrogen Gas Analysis* (*TCD*)

A 10 port gas-sampling valve may be used with nitrogen or argon as carrier gas. Nitrogen or argon gas is to be used to ensure that the hydrogen ‘peak’ remains positive. By using any column or multiple columns helium and hydrogen are separated and also these components are separated from the other components of the sample. Typically a dedicated TCD is used to analyse hydrogen. Manufacturer’s instruction is to be followed to estimate hydrogen and helium.

NOTE — When helium is not expected the resolution of hydrogen from helium is not important.

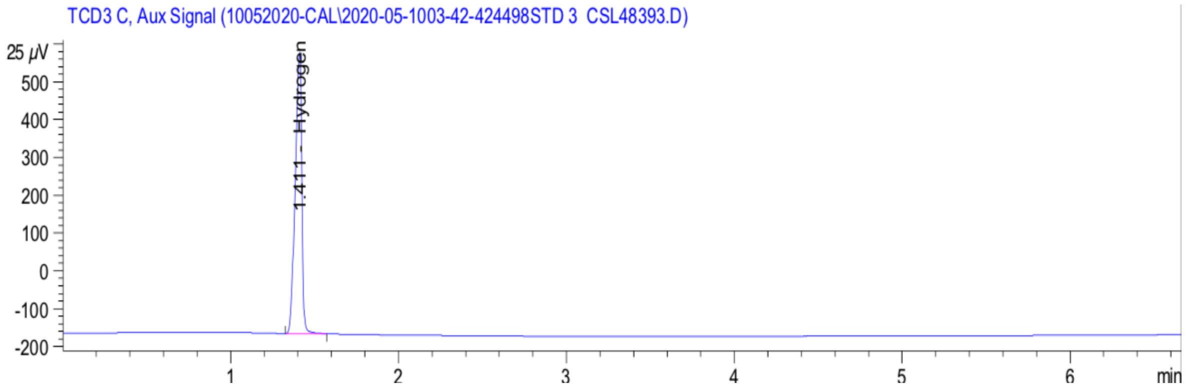

FIG. 2 HYDROGEN CHROMATOGRAM FROM TCD-3

4.4.5 *Hydrocarbon Gas Analysis* (*FID*)

A 6 port gas-sampling valve in combination with a 6-port pre-column switching backflush valve for C_{6+} is used in refinery gas analyser. These valves are housed in a heated enclosure and the temperature is maintained as per manufacturer's directive to prevent the condensation of C_{6+} components in the sample.

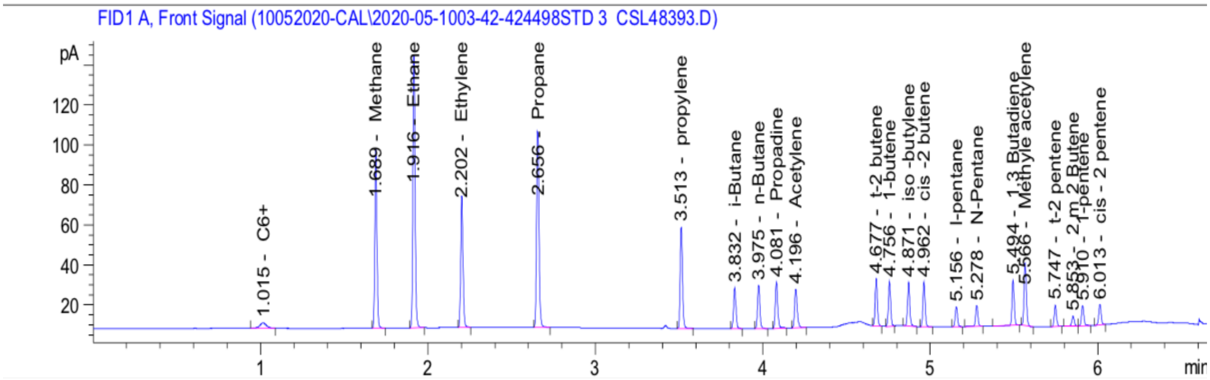

FIG. 3 HYDROCARBON CHROMATOGRAM FROM FID

4.4.6 *Non-Hydrocarbon Gases*

A 10 port gas-sampling valve in combination with 6 port valve using helium or hydrogen gas as carrier gas to detect O_2, N_2, CO_2 and CO by using any column or multiple columns. Also lighter hydrocarbon gases CH_4, C_2H_6 can be analysed through TCD detection from the stated column/columns.

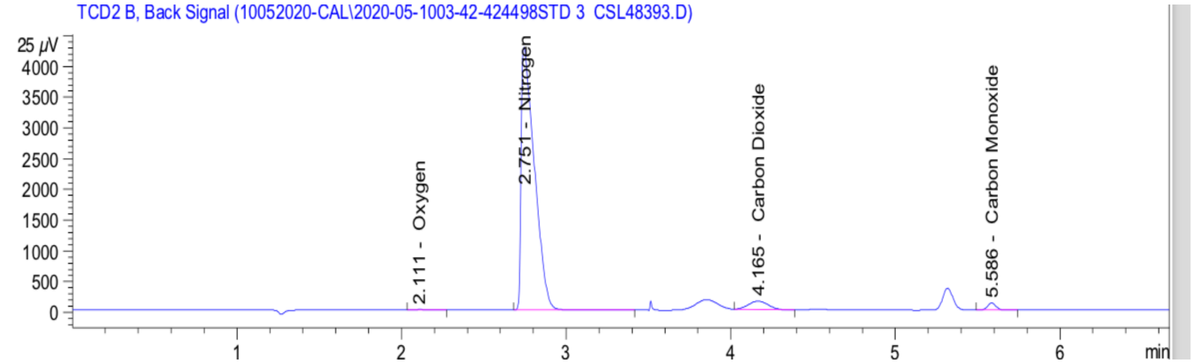

Fig. 4 Non-Hydrocarbon gases chromatogram from TCD-2

4.4.7 *Column Series/Reversal Switching Valve*

A multiport valve may be used to provide the C_{6+} for this analysis. Manufacturer's manual is to be followed for this configuration details.

> NOTE — If dimethylsilicone capillary is the column, the same column may be used to elute all hydrocarbon compounds using temperature programming without backflush operation.

4.4.8 *Gas Controls*

The gas chromatograph is to be provided with suitable facilities for delivery and control of carrier gases and detector gases. All these requirements are to be provided as per instrument manufacturer.

4.4.9 *Analytical Columns*

A typical refinery gas analyser (Fig. 1) contains the following analytical columns.

4.4.9.1 *Column* 1 — 0.61 m length, 2 mm inner diameter, 3.175 mm outer diameter, stainless steel material with silica gel beads

4.4.9.2 *Column* 2 — 1.22 m length, 2 mm inner diameter, 3.175 mm outer diameter, stainless steel material with silica gel beads

4.4.9.3 *Column* 3 — 2.44 m length, 2 mm inner diameter, 3.175 mm outer diameter, stainless steel material with molecular sieve 0.5 nm

4.4.9.4 *Column* 4 — 1 m length, 2 mm inner diameter, 3.175 mm outer diameter, stainless steel material with porous polymer absorbent

4.4.9.5 *Column* 5 — 2.44 m length, 2 mm inner diameter, 3.175 mm outer diameter, stainless steel material with molecular sieve 0.5 nm

4.4.9.6 *Column* 6 — 15 m length, 0.32 mm inner diameter, 5µm film, polysiloxane phase

4.4.9.7 *Column* 7 — 25 m length, 0.32 mm inner diameter, 8µm film, Al_2O_3S phase

4.4.9.8 *Column* 8 — 0.45m length, 0.32mm inner diameter, 8µm film, fused silica phase

NOTE — Column details and reactivation procedure will be available from the supplier.

5 REAGENTS AND MATERIALS

All chemicals are of reagent grade unless specified otherwise, and all water used is distilled or deionized.

5.2 Carrier Gases

Gas purifiers to remove oxygen and moisture are to be installed at the inlet to the gas chromatograph for all carrier gases.

5.2.1 *Chromatographic Grade Hydrogen* — 99.995 percent minimum purity, <0.1 ppm H_2O

5.2.2 *Chromatographic Grade Helium* — 99.995 percent minimum purity, <0.1 ppm H_2O

5.2.3 *Chromatographic Grade Nitrogen* — 99.995 percent minimum purity, <0.1 ppm H_2O

5.3 FID Detector Gases

5.3.1 *Chromatographic Grade Hydrogen* — 99.995 percent minimum purity

5.3.2 *Chromatographic Grade Air* — Less than 10 ppm-mol each of total hydrocarbons and water.

5.4 Calibration Standards

Individual and mixed component reference standards are available commercially and may be used to calibrate the instrument. The calibration standard mixture should be prepared gravimetrically and supplied with both gravimetric and calculated volumetric and mole percent concentrations and to be NIST traceable. The calibration standard mixture should have analytical uncertainty of <1 percent relative.

5.5 Secondary Reference Standards

A mixture or mixtures of known composition that is (are) independent of the calibration standards and similar wherever possible in concentration to the samples being analyzed. The secondary reference standards are used as check standards to monitor testing precision and accuracy.

6 PREPARATION OF APPARATUS

Manufacturer’s operating manual is to be followed to make the analyzer ready for testing.

7 CALIBRATION AND STANDARDIZATION

7.1 After the installation of the analyzer and at least yearly thereafter, retention times of the components of reference standards are determined. The order of elution and the detections from TCD and FID detectors are verified as per the guideline of the analyzer manufacturer.

7.2 The linearity of the response of the component of interest is verified using at least three concentrations of the analytes bracketing the expected concentration of the analyte. The linearity regression coefficient of the component should be at least 0.999. For low concentration points separate calibration may be required if linearity criteria is not achieved. Linearity should be confirmed annually.

7.3 After the linearity is established a single calibration standard may be used to calibrate and recalibrate periodically or after any hardware change or the failure of QC check. Experimental response factors are determined for each component of the calibration standard which is tested under the same conditions of pressure and temperature as the sample. Response factors are calculated according to Eq. 1.

$$RF_i = C_i / A_i \qquad (1)$$

Where

RF_i = the response factor of component i;

C_i = the known concentration of i;

A_i = the integrated area of peak i.

The response factor of C_{6+} when backflushed as one composite is estimated as follows.

$$RF_{C6+} = RF_{C5AV} \times (72/93) \qquad (2)$$

Where

RF_{C6+} = the response factor C_{6+}

RF_{C5AV} = the average response factors of i-C_5 and n-C_5

NOTES

1 When urging the valve, sample loops and the inlet systems with calibration standards, high flow is to be avoided as the high flow may change the composition of the standard mixture, the typical purging flow should be approximately 10-30 mL/min.

2 Standards containing hydrogen sulphide should use corrosive resistant regulators. Vents from the gas sampling valve to be vented to a well-ventilated hood to avoid the exposure to hydrogen sulphide.

3 Hydrocarbons with a boiling point greater than isopentane in the standard have a potential for condensation. Proper size and the pressure of the calibration gas cylinders are to be fixed in consultation with the gas standard manufacturer.

8 QUALITY MONITORING

Secondary check standard(s) that approximates composition of samples being analysed is to be run periodically to assure the accuracy of the analysis. Results should agree within 2 percent relative of the certified value for components present at > 5 volume percent.

9 SAMPLING

9.1 Introduction of the sample into a chromatograph must be done in a manner to ensure the injection of representative sample from the sample container, Improper sample introduction will lead to the less precision and inaccurate results.

9.2 Higher boiling components such as C_{5+} may condense during sampling at the process unit if the sample vessel is not at the same or higher temperature than sample stream. This will result inaccurate collection of the sample.

9.3 If the hydrocarbon dew point is lower than the temperature at which the sample is exposed, the sample is not required to heat for sample introduction to the chromatograph. If the sample is expected to contain hydrocarbons heavier than C_{5+}, the sample is to be heated prior to the introduction to gas chromatograph.

9.4 Connections from sample container to the sample inlet should be of stainless tubing, copper, vinyl and rubber tubing are not to be used.

9.5 Samples should be clean and free of liquid prior to injection. It is better to use filters between sample vessel and analytical instrument to minimize the risk and damage to the instrument.

10 PROCEDURE

10.1 Orient the sample vessel in vertical condition.

10.2 Connect the sample from the sample vessel to the gas chromatograph sample inlet through the evaporator, if heavier hydrocarbons (> C_{5+}) is expected in the sample.

10.3 Purge the sample injection system sufficiently to purge out the trapped gases with flow in the range 50 – 70 mL/min.

10.4 Stop the purging and start the analysis at zero sample flow at the outlet.

10.5 Take the Chromatograph output, review the results and report.

11 CALCULATION

11.1 Calculate the concentration of each component according to the following equation:

$$S_{C_i} = R_{F_i} \times S_{A_i} \quad (3)$$

Where

S_{C_i} = concentration of component *i* in the sample;

R_{F_i} = response factor for component *i*;

S_{A_i} = integrated area for peak *i*.

11.2 Determine the total amount of all components by summing the component concentrations.

11.3 The sum of all component concentrations from **11.1** must be within 100 ± 5 percent.

11.4 Normalize the final results to 100 percent.

12 REPORTING

Report the concentration of each component as mole percent nearest to 0.01 percent

13 PRECISION

13.1 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials.

13.1.1 The Repeatability (r) is <1 percent.

13.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials.

13.2.1 The Reproducibility (R) is not established for this test method.

ANNEX A

(*Clause* 2)

RECOMMENDED OPERATING CONDITIONS

A-1 TYPICAL GC CONDITIONS FOR REFINERY GAS ANALYSER

Valve temperature	120°C

Oven temperature program	60ºC hold 1 min, to 80ºC at 20ºC/min, to 190ºC at 30ºC/min

A-2 FID CHANNEL

Front inlet	150ºC, split ratio 30:1 (uses higher or lower split ratio according to the concentrations of hydrocarbons)
Column	6 and 7
Column flow (He)	3.3 ml/min (0.89 kg/cm^2 at 60ºC), constant flow mode

A-3 FID

Temperature	200ºC
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40 mL/min

A-4 SECOND TCD CHANNEL

Column	1, 2 and 3
Column flow (He)	25 ml/min (2.53 kg/cm^2 at 60ºC), constant flow mode
Precolumn flow (He)	22 ml/min (0.49 kg/cm^2 at 60ºC), constant pressure mode

A-5 TCD

Temperature	200ºC
Reference flow	45 ml/min
Make up	2 ml/min

A-6 THIRD TCD CHANNEL

Column	4 and 5
Column flow (N_2)	24 ml/min (1.82 kg/cm^2 at 60ºC), constant flow mode
Precolumn flow (N_2)	24 ml/min (0.49 kg/cm^2 at 60ºC), constant pressure mode

A-7 TCD

Temperature	200ºC
Reference flow	30 ml/min
Make up	2 ml/min