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BUREAU OF INDIAN STANDARDS
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Draft Indian Standard

Quantitative determination of Dimethyl ether (DME) content in DME- Liquefied petroleum gas (LPG) blended fuel by Gas Chromatography

(ICS 75.100)

Methods of Test for Petroleum, Petroleum Products (including gaseous fuels) and Lubricants Sectional Committee, PCD 01	Last date for receipt of Comments is 01 February 2023

FOREWORD

(*Formal clauses will be added later*)

Liquefied Petroleum Gas (LPG) is being used in India to cater the fuel needs of domestic, commercial and industrial sectors apart from use as automotive fuel. The consumption of LPG is ever increasing in the country. This necessitates use of alternate fuels to partially substitute LPG with fuel such as dimethyl ether (DME). It is the simplest ether with oxygen connecting two methyl groups having no c-c bond. DME can be blended with LPG by 20 percent by weight and the blended fuel can be used for cooking in households and other applications.

As there is no Indian Standard available for determination of Dimethyl ether (DME) content in DME – Liquefied petroleum gas (LPG) blended fuel. Hence, this method developed for quantitative determination of Dimethyl ether (DME) content in DME – Liquefied petroleum gas (LPG) blended fuel by Gas Chromatography.

The composition of the Committee, responsible for the formulation of this standard is given at Annex

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 : 2022 ‘Rules for rounding off numerical values (*second revision*)’.

1 SCOPE

1.1 This standard prescribes a method for quantitative determination of Dimethyl ether (DME) content in DME - Liquefied petroleum gas (LPG) blended fuel by Gas Chromatography. Component concentrations are determined in the range of 10 mass percent to 100 mass percent.

1.2 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 prior to use.

2 REFERENCES

The following Standards contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication the editions indicated were valid. All standards are subjected to revision and parties to agreements based on this standard are advised to use the latest editions of the standards indicated below:

IS No.	*Title*
1447 (Part 2) : 2013	Methods of sampling of petroleum and its products : Part 2 Sampling of liquefied petroleum gases (LPG) *(second revision)*
1448	Methods of test for petroleum and its products
[P 71] : 2004/ ISO 4256:1996	Part 71 Liquefied Petroleum Gases - Determination of Gauge Vapour Pressure - LPG Method
[P 72] : 1968	Part 72 Volatility of liquefied petroleum gases
[P 76] : 2019	Methods of Test for Petroleum and its Products [P : 76] Liquified Petroleum Gases and Light Hydrocarbons — Determination of Density or Relative Density — Pressure Hydrometer Method (*first revision*)
[P 151] : 2004/ISO 7941:1998	Part 151 Commercial propane and butane - analysis by gas chromatography
3196 (Part 1) : 2013	Welded Low Carbon Steel Cylinders Exceeding 5 Litre Water Capacity for Low Pressure Liquefiable Gases - Part 1 : Cylinders for liquefied Petroleum Gases (LPG) (*sixth revision*)
16704 : 2018/ISO 16861 : 2015	Petroleum Products – Fuels (Class F) – Specifications of Dimethyl Ether (DME)
4576:2021	Liquefied Petroleum Gases – Specification (*fourth revision*),

3 TERMINOLOGY

For the purpose of this standard, the following definition shall apply.

3.1 Liquefied Petroleum Gas (LP Gas or LPG)

The term applies to a mixture of certain light hydrocarbons derived from petroleum which are gaseous at normal ambient temperature and atmospheric pressure but may be condensed to the liquid state at normal ambient temperature by the application of moderate pressure.

3.1.1 LP gases mainly consist of one or more of the following hydrocarbons:

a) Propane (C_3H_8)
b) Propylene ($C_3 H_6$)
c) n-butane ($C_4 H_{10}$)
d) Iso-butane (C_4H_{10})
e) Butylene (C_4H_8)

3.1.2 Small quantities of one or more of the following hydrocarbons may also be present:

a) Ethane (C_2H_6)
b) Ethylene (C_2H_4)
c) Pentane (C_5H_{12})
d) Pentene (C_5H_{10})

3.2 Di Methyl Ether (DME) confirming to IS 16704: 2018/ISO 16861: 2015

4 SUMMARY OF THE TEST METHOD

4.1 Outline of the method

DME-LPG blended sample is analyzed via gas sampling valves by gas chromatography and compared to corresponding components separated under identical operating conditions from pure DME reference standard. The chromatogram of the sample is interpreted by comparing peak retention times and areas with those obtained for the pure DME reference standard.

4.2 Apparatus

4.2.1 *Gas Chromatograph (GC)*

Any gas chromatographic instrument provided with a linear temperature programmable column oven. Multi-step column oven temperature programming is required, consisting of an initial hold time, an initial temperature program followed by an isothermal temperature hold and another programmed temperature rise. The temperature control must be capable of obtaining a retention time repeatability of 0.05 min throughout the scope of this analysis. A flame ionization detector (FID) having sensitivity of 0.5% (mole) or less for the DME compound is strongly recommended.

4.2.2 *Data Acquisition*

Any commercial integrator or computerized data acquisition system may be used for display of the chromatographic detector signal and peak area integration. The device should be capable of calibration and reporting of the final response corrected results.

4.2.3 *Sample Introduction*

For gas sampling, a six-port gas sampling valve (GSV) with a 250 µL fixed sampling loop may be provided. This valve shall be contained in a heated enclosure and operated at a temperature above the boiling point of the highest boiling component in the sample.

4.3 Gas Controls

The GC shall be provided with suitable facilities for delivery and control of carrier gas and the detector gases. This will consist of the appropriate tank and downstream regulators and supply tubing as well as the mass or pressure controls for the precise regulation of the instrument operation.

4.4 Columns

Condition all columns used according to the manufacturers' suggestions prior to use. The recommended analytical column for this test method is 100m length, internal diameter 0.25mm and film thickness 0.5µm of 100% dimethylpolysiloxane capillary column.

5 REAGENTS AND MATERIALS

5.1 Carrier Gases

For carrier gases, it is recommended to install commercial active oxygen scrubbers and water dryers, such as molecular sieves, ahead of the instrument to protect the system's chromatographic columns. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

5.1.1 *Helium* — 99.995 Percent minimum purity, <0.1 ppm H2O. The use of appropriate scrubbers may be sufficient to obtain the desired purity.

5.2 Detector Gases

5.2.1 *Hydrogen* — 99.995 Percent minimum purity. The use of appropriate scrubbers may be sufficient to obtain the desired purity.

NOTE — Hydrogen is a flammable gas under high pressure.

5.2.2 *Nitrogen* — 99.995 Percent minimum purity. The use of appropriate scrubbers may be sufficient to obtain the desired purity.

5.2.3 *Air* — less than 10 ppm each of total hydrocarbons and water. The use of appropriate scrubbers may be sufficient to obtain the desired purity.

NOTE — Improper handling of compressed gas cylinders containing air, nitrogen, hydrogen, or helium can result in an explosion. Rapid release of nitrogen or helium can result in asphyxiation.

5.3 Reference Standards

5.3.1 *Purity of Reagents*

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3.2 *Reference DME standard*

Analytical grade DME reference standard commercially available and may be used to establish quantitative determination of DME content in DME-LPG blended fuel.

6. PREPARATION OF APPARATUS

6.1 Set up the instrumentation in accordance with the manufacturer’s instructions or as specified herein.

6.2 Install and condition the column according to manufacturer’s instructions.

6.3 Set the GC instrument to the operating parameters. Allow the instrument to stabilize before proceeding with calibration and sample injections. Typical operating conditions for 100 Percent dimethylpoly siloxane column are provided in Table **1**.

Table 1 Typical Operating Condition
(*Clause* **6.3)**

Column	100 m X 0.25 mm X 0.5 µm of 100% Dimethyl polysiloxane
Carrier Gas	Helium
Carrier Gas flow	2.0 mL/min
Injector temperature	250°C
Injection type	Split with split ratio 150:1
Purge flow	3.0 mL/min
Injection volume	250 µL
Oven program	Initial temperature 35°C for 10 minute; First Ramp at 2.5°C/minute to 120°C hold for 0 minutes Second Ramp at 15°C/minute to 220°C hold for 5 minutes
Detector	FID Temperature: 250°C Hydrogen flow: 40 mL/minute Air flow: 400 mL/minute Make-up gas: Nitrogen Make-up gas flow: 30 mL/minute
Analysis time	55.6 min

6.4 Obtain duplicate chromatograms of the standard or sample, or both. Ensure that none of the peaks obtained have exceeded the upper range limit of the data handling device (at full scale on the data handling device, all peaks are on scale and display symmetrical, Gaussian shapes as opposed to flat peak tops). Use the same sample size (split ratio) and range for all runs. Example chromatograms are provided in Fig. **1**.

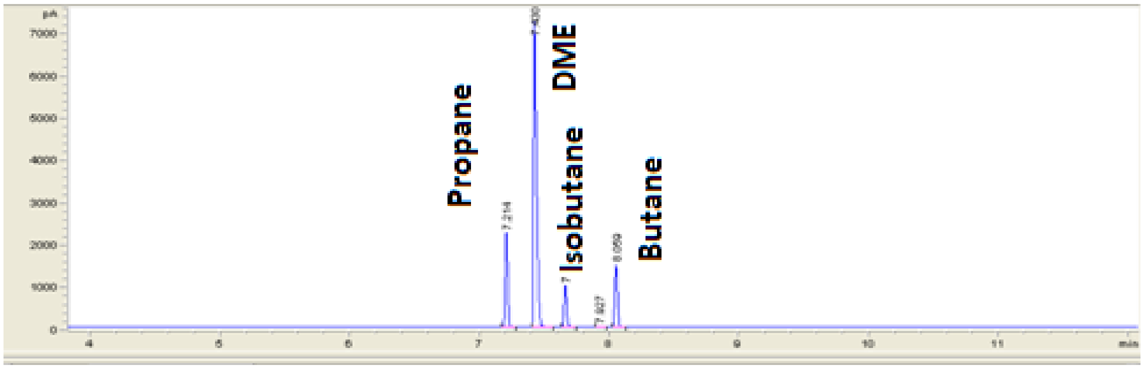

Fig 1 — Example Chromatogram Using the Dimethylpolysiloxane Column

6.5 Gas Sampling Valve

Set valve on and off times to comply with manufacturer’s instructions

7 CALIBRATION AND STANDARDIZATION

7.1 Qualitative

Determine the retention time of DME by analyzing known reference standard in the same manner as the samples. Typical retention time of DME is 7.48 min.

7.2 Quantitative

Determine the quantity of DME in DME-LPG blended fuel is interpreted by comparing peak areas with those obtained for the pure DME reference standard.

8 PROCEDURE

8.1 Sampling

Sampling at the sample source and at the chromatograph shall always be done in a manner that ensures that a representative sample is being analyzed. Lack of precision and accuracy in using this test method can most often be attributed to improper sampling procedures.

8.2 Gas Sample Valve Injection

Flush a gas sample loop with 5 to 10 mL of standard and sample (approximate 45s time), close cylinder valve, and allow the sample pressure to equilibrate to atmospheric pressure (stopped flow) before introducing the sample into the carrier gas stream.

8.3 Sample Analysis Procedure

8.3.1 Adjust the instrument operating variables to the values specified in Table **1.**

8.3.2 Equilibrate the chromatographic system and inject the air blank until a representative chromatogram is obtained.

8.3.3 Inject an appropriate size DME reference standard (as determined in Table **1**) into the injection port and start the analysis. Obtain a chromatogram and a peak integration report. Repeat the same standard for six times consecutively.

8.3.4 Inject a minimum of one air blank to check for carryover after six DME reference standards.

8.3.5 Inject an appropriate size sample (as determined in Table **1**) into the injection port and start the analysis. Obtain a chromatogram and a peak integration report. Repeat the sample in duplicate.

8.3.6 Inject DME standard throughout the analysis, with a minimum of one injection at the end of sequence. One injection after every sixth sample analysis is recommended.

8.3.7 Record the peak area response for each analyte of interest, if present. Note all observed peaks in the blank injection and exclude these as artifacts from any calculation.

9 SYSTEM SUITABILITY

9.1 The % RSD for peak area response of DME from the first six injections of the DME standard should be ≤ 10 Percent.

9.2 The % RSD for peak area response of DME from all injections of the DME standard throughout the analysis should be ≤ 10 Percent.

10 CALCULATION

10.1 Identify DME peak by matching retention times with those for known reference standards. Obtain the area for DME peak.

$$\text{DME content (Percent m/m)} = (A_{\text{sample}}/A_{\text{standard}}) \times \text{purity of standard}$$

A_{sample} = Peak area of DME in sample

$A_{standard}$ = Mean peak area of DME in first six standard injections

11 REPORT

11.1 Report the concentration of DME component as Percent (m/m), to the nearest 0.1 Percent (m/m).

12 PRECISION

12.1 Repeatability

The difference in two test results obtained by the same operator with the same apparatus in a given laboratory under constant operating conditions on test samples taken from the same laboratory sample should, in the long run in the normal and correct operation of the test method not exceed the values given in Table **2**.

TABLE 2
(*Clause* **12.1**)
Repeatability values of the method obtained with the 20% DME-80% LPG blended fuel.

S No	**20% DME+80% LPG blended fuel (%m/m)**	**Calculated DME content (%m/m)***	**% RSD**
1	18.5% DME standard	18.1	3.6

NOTE — Calculated average value of 6 replications