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Draft Indian Standards

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS PART DETERMINATION OF OXYGENATES SUCH AS ETHERS, TERTIARY AMYL ALCOHOL AND C₁ TO C₄ ALCOHOLS IN MOTOR GASOLINE BY GAS CHROMATOGRAPHY METHOD

(ICS No. 75.100)

Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee PCD 01	Last date for receipt of comment is 31 October 2023

FOREWORD
(*Formal clause will be added later*)

This standard elucidates the procedure for determination of oxygenates in term of ethers and alcohols in motor gasoline using gas chromatography technique. The detailed calibration of oxygenates with required standard for preparation is explained in method.

In the preparation of this standard, considerable assistance has been derived from ASTM D 4815-15b (2019)- Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography.

In reporting the results of a test 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 the method of test for determination of ethers and alcohols in gasolines by gas chromatography, such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), *diiso*-propyl ether (DIPE), methanol, ethanol, *iso*-propanol, *n*-propanol, *iso*-butanol, *tert*-butanol, *sec*-butanol, *n*-butanol, and *tert*-pentanol (*tert*-amyl alcohol).

1.2 The method covers the measurement range from 0.20 mass percent to 20.0 mass percent of individual ethers and from 0.20 mass percent to 12.0 mass percent of individual alcohols.

1.3 This standard also describes the calculation of individual components to convert to volume percent and to oxygen in mass percent.

NOTES

1 Appropriate calibration plot may be used for different concentration range.

2 For samples with higher concentration dilution technique with suitable solvent may be adopted during measurement.

3 Hydrocarbons may interfere with several ethers and alcohols at concentrations of <0.20 mass percent. The reporting limit of 0.20 mass percent was established for gasolines containing a maximum of 10 volume percent olefins and gasolines containing >10 volume percent olefins, the interference may be > 0.20 mass percent. Annex A provides a chromatogram presenting the interference noticed with a gasoline containing 10 volume percent olefins.

1.4 Alcohol-based fuels, such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol, are specifically excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

2 REFERENCES

The following standards contain provisions which, through reference in text constitute provisions of this standard. At the time of publication, the editions indicated were valid. All the standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below.

IS No.	Title
IS 1447 (Part 1) : 2021	Methods of Sampling of Petroleum and its Products Part 1 Manual Sampling (*second revision*)
IS 1448 (Part 16)/ ISO 3675 : 1998	Methods of test for petroleum and its products Part 16 Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method (*fourth revision*)
IS 1448 (Part 167) : 2018/ ISO 12185	Methods of test for petroleum and its products Part 167 determination of density — Oscillating U — Tube method
ASTM D 4307 : 2017	Standard Practice for preparation of liquid blends for use as analytical standards

3 TERMINOLOGY

3.1 Oxygenates — Organic compounds which contain oxygen. Examples are alcohols and ethers.

4 PRINCIPLE

Gas chromatography is an analytical technique based on separation of components using their difference in physical and chemical interactions with the stationary phase during elution through a column. GC technique is employed to separate components of mixture into their individual components with suitable column using two immiscible phases — mobile phase and stationary phase. The separated components are detected by a flame ionization or thermal conductivity detector and the concentration of each component is calculated with reference to the internal standard method calibration.

5 REAGENTS AND MATERIALS

5.1 Carrier Gas — Helium with minimum purity of 99.99 mol percent.

5.2 Detector Fuels — Hydrogen and Zero Air with minimum purity of 99.95 percent, if FID is used as detector.

> NOTE — Suitable carrier gas such as Hydrogen and Nitrogen may also be selected as per OEMs recommendation and detector choice.

5.3 Standards for Calibration and Identification

Standards of all components such as Ethanol, Methanol, Isopropanol, *tert*-Butanol, *n*-Propanol, MTBE, *sec*-Butanol, DIPE, Isobutanol, ETBE, *ter*t-Pentanol, *n*-Butanol, TAME to be analyzed and the internal standard DME (1, 2-Dimethoxy Ethane), required to identify the retention time of all components to calibrate gas. Chromatograph for quantitative analysis. All components must have purity more than 99.9 percent and free of the other impurities, which would not interfere with standard components.

6 APPARATUS

6.1 Gas Chromatographic

Standard gas chromatographic system is required, which is capable of resolving the individual ethers and alcohols that are presented in Table 1. A gas chromatographic instrument, which can be operated at the conditions given in Table 2 and has a column switching cum back flushing system equivalent to Fig. 1 chromatographic resolution, has been found acceptable for this analysis. Flow controllers with pressure control devices shall be capable of precise control of required low flow rates and pressure control (*see* Table 2).

Table 1 Relevant Physical Constants and Retention Time of Compounds
(*Clauses* 6.1 and 9.2)

SI No.	Component	Retention Time Min.	Relative Retention Time		Molecular Mass, g/mol	Relative Density at 15.56/15.56ºC
			MTBE = 1	DME = 1		
(1)	(2)	(3)	(4)	(5)	(6)	(7)
i)	Methanol	3.180	0.6	0.4	32.0	0.7963

ii)	Ethanol	3.563	0.7	0.5	46.1	0.7939
iii)	Isopropanol	3.940	0.8	0.5	60.1	0.7899
iv)	*tert*-Butanol	4.298	0.8	0.6	74.1	0.7922
v)	*n*-Propanol	4.748	0.9	0.7	60.1	0.8080
vi)	MTBE	5.227	1.0	0.7	88.2	0.7460
vii)	*sec*-Butanol	5.635	1.1	0.8	74.1	0.8114
viii)	DIPE	6.025	1.2	0.8	102.2	0.7282
ix)	Isobutanol	6.343	1.2	0.9	74.1	0.8058
x)	ETBE	6.562	1.3	0.9	102.2	0.7452
xi)	*tert*-Pentanol	6.808	1.3	0.9	88.1	0.8170
xii)	1,2 Dimethoxyethane(DME)	7.224	1.4	1.0	90.1	0.8720
xiii)	*n*-Butanol	7.560	1.4	1.0	74.1	0.8137
xiv)	TAME	8.752	1.7	1.2	102.2	0.7758

Table 2 Chromatographic Operation Conditions for TCEP/WCOT Column
(*Clause 6.1*)

SI No. (1)	Temperatures (2)	°C (3)	Flows (4)	ml/min (5)	Carrier Gas : Helium (6)	
i)	Column Oven	60	to injector	33	Sample size, µl	0.5–2
ii)	Injector	240	Column	5	Split ratio	5:1 to 15:1
iii)	Detector - TCD	200	Auxiliary	3	Backflush, min	0.2–0.35
iv)	Detector - FID	250	Makeup	20	Valve reset time	8–10 min

6.1.1 *Detector*

A TCD (thermal conductivity detector) or FID (flame ionization detector) can be used with sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 volume percent concentration of an oxygenate.

6.1.2 *Switching and Back flushing Valve*

A valve designed to be with a low volume design and capable of performing the function as per the method requirements shall be suitably located inside the gas chromatographic column oven. The valve shall execute all the functions described in **9.1** to produce a chromatogram as illustrated in Fig.1.The functioning of valve shall not weaken the chromatograph significantly.
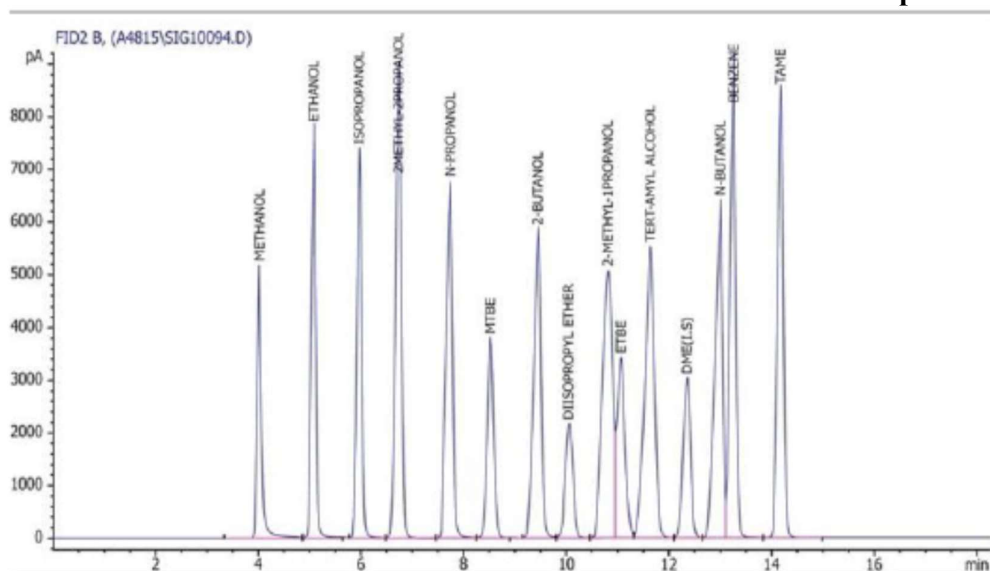
FIG. 1 OXYGENATES CHROMATOGRAPH IN GASOLINE

6.1.2.1 *Valco Model No. A 4C10WP* — 1.6 mm (1∕16 in.) fittings

6.1.2.2 *Valco Model No. C10W* — 0.8 mm ($\frac{1}{32}$ inch) fittings. This valve is suitable for use with columns of 0.32 mm inside diameter or smaller.

6.1.2.3 If the gas chromatograph is equipped with an auxiliary oven, the valve and the polar column can be placed inside the same. In such a configuration, the nonpolar column is located in the main oven and the temperature can be adjusted to optimize resolution of oxygenates.

6.1.3 *Automatic Valve Switching Device*

Must be used, which would be able to synchronize with injection and data collection times to ensure repeatable switching times.

6.1.4 *Injection System*

Split injector should be installed, if capillary columns or FID are used. Split injection is necessary to maintain the actual sample size within the limits of column and detector optimum efficiency and linearity. Specific gas chromatographs are equipped with on-column injectors and auto samplers, which can inject small samples sizes.

6.1.4.1 Liquid sampling valves with auto sampling injector equipped microliter syringe have been used successfully for introducing representative samples into the GC inlet.

6.2 Data Analysis

6.2.1 *Recorder*

A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less can be used to monitor detector signal. Full-scale response time should be 1s or less with sufficient sensitivity and stability to meet the requirements of detector.

6.2.2 *Integrator*

Shall be provided to determine the detector response and peak heights or areas can be measured by computer, electronic integration, or manual techniques.

6.3 GC columns

6.3.1 *Polar Column*

Pre-separation of oxygenates from volatile hydrocarbons performs by this column in the same boiling point range. The oxygenates and remaining hydrocarbons are back flushed to the nonpolar column mentioned below in **6.3.2**. Any column with equivalent or better chromatographic efficiency and selectivity to that described in **6.3.1.1** can be used. The column shall perform at the same temperature as required for the column in **6.3.2**, except if located in a separate auxiliary oven as in **6.1.2.3**.

6.3.1.1 *TCEP Micro-Packed Column*

560 mm (22 inch) L × 1.6 mm (1⁄16 inch) OD x 0.76 mm (0.030 inch) ID stainless steel tube packed with 0.14 g to 0.15 g of 20 percent (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW).

6.3.2 *Nonpolar Column*

Any analytical column with equivalent or better chromatographic efficiency and selectivity to that described in **6.3.2.1** and illustrated in Fig. 2 can be used.

6.3.2.1 *WCOT Methyl Silicone Column*

30 m (1181 inch) L × 0.53 mm (0.021 inch) ID fused silica WCOT column with a 2.6 μm film thickness of cross-linked methyl siloxane.
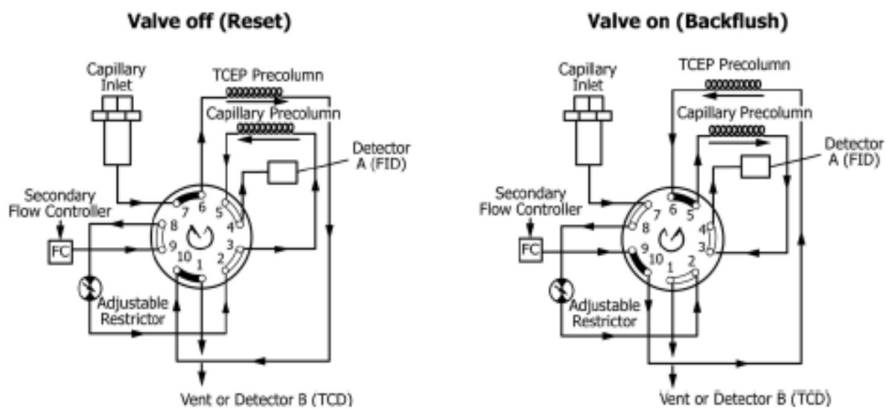
FIG. 2 VALVE SWITCHING POSITION DIAGRAM FOR ANALYSIS OF OXYGENATES IN GASOLINE

6.4 Volumetric Glassware

Class A pipettes, burettes, one-mark volumetric flasks and measuring cylinders as required for the preparation of solutions and standard blends.

> NOTE — All volumetric measurements shall be made at the calibration temperature (normally 20 °C) of the volumetric glassware used ± 2 °C. Deviation from this will lead to inaccurate mass/volume relationships.

6.5 Analytical Balance — Capable of weighing to the nearest 0.1 mg.

6.6 Refrigerator

Suitable for storing flammable liquids that are protected internally to prevent ignition of flammable vapors.

7 SAMPLING

Samples shall be taken by the procedures described in IS 1447 (Part 1) or its equivalent, when obtaining samples from storage tank or pipelines. Upon receipt in the laboratory, chill the sample in its original container to 0 °C to 5 °C (32 °F to 40 °F) before any sub sampling is performed and later, transfer the chilled sample to a vapor tight container and store at 0 °C to 5 °C (32 °F to 40 °F) until needed for analysis.

8 PREPARATION OF CALIBRATION STANDARDS

8.1 Prepare a minimum of five standards for full range multi component calibration as 0.1, 0.5, 2.5, 10, 15, and 20 mass percent of each oxygenate shall be used for concentration range of interest.

8.2 First determine the purity of the oxygenate stocks and apply for the impurities correction. Whenever possible, use stocks of at least 99.9 percent purity.

8.3 Prepare standards by transferring a fixed volume of oxygenates, using pipettes or droppers (for volumes below 1 volume percent), to 100 ml volumetric flasks or septum capped vials as follows. Cap and record the tare weight of the volumetric flask or vial to 0.1 mg. Remove the cap and carefully add the oxygenate to the flask or vial. Cap and record the net mass (W_i) to 0.1 mg of the oxygenate added. Follow the same procedure for each oxygenate of interest. Similarly, add 5 ml of the internal standard (DME) and record its net mass (W_s) to 0.1 mg.

8.4 Dilute each standard to 100.0 ml with oxygenate free gasoline or a mixture of hydrocarbons, such as isooctane/ mixed xylenes (63.35 volume percent). Do not exceed 30 volume percent for all oxygenates, including the internal standard added.

NOTE — To minimize evaporation of light components, chill all chemicals and gasoline or solvent used to prepare standards. Store the capped calibrations standards below 5 °C (40 °F) when not in use.

9 CALIBRATION

9.1 Instruments Settings and Conditions

9.1.1 *Instrument*

Use low volume connectors and narrow bore tubing to connect the both column to the injector, detector, valve system and then adjust the operating conditions as listed in Table 2. Check the system for leaks before proceeding further.

NOTE — Minimize the volume of the chromatographic system that comes in contact with the sample to avoid peak broadening. Do not turn on the detector circuits before leak check. If different columns with different diameter are used than adjust the optimum flows and temperatures as per requirement.

9.1.2 *Flow Rate Adjustment*

9.1.2.1 In the RESET position of valve connect a flow meter to the column vent and adjust the pressure 5.0 ml∕min flow (14 psig) to the injector port. Soap bubble flow meters are suitable.

9.1.2.2 Connect the flow meter to split injector vent and adjust the flow of 70 ml /min. using 'A- flow controller' and recheck the column vent flow set in **9.1.2.1** if necessary.

9.1.2.3 Switch the valve to the Backflush position and adjust the variable restrictor to give the same column vent flow set in **9.1.2.1** to minimize flow changes when the valve is switched.

9.1.2.4 Switch the valve to the inject position (RESET) and adjust the flow of 3.0 ml/min to 3.2 ml/min at the detector end by 'B-flow controller'. Add makeup flow or TCD switching flow as per application requirement to get total of 21 ml/min at the detector end.

9.1.2.5 When a TCD is used, turn on the filament current and allow the detector to equilibrate. When a FID is used, set the hydrogen and air flows and ignite the flame.

9.1.3 *Backflush Timing Determination*

The start time of the integrator and valve timer must be synchronized with the injection to reproduce the Backflush time precisely by experiment as follows.

9.1.3.1 The correct BACKFLUSH time is determined experimentally by using valve switching times between 0.20 min and 0.35 min. Start trial with a valve BACKFLUSH time of 0.23 min. and inject 1 μL to 3 μL of a blend containing at least 0.5 percent or greater oxygenates, and simultaneously begin timing observation of the analysis. At 0.23 min, rotate the valve to the BACKFLUSH position and leave it until the complete elution of TAME is observed. Record this time as the RESET time, when the valve is returned to the RESET position. When all of the remaining hydrocarbons are back flushed, the signal will return to a stable baseline and the system is ready for another analysis. The chromatogram should appear similar to the one illustrated in Fig.1.

9.1.3.2 Ensure that the BACKFLUSH time is sufficient to quantitatively transfer the higher concentrations of the ethers into the nonpolar column specially MTBE.

9.1.3.3 Use a standard blend of oxygenates to optimize the valve BACKFLUSH time. When the valve is switched too shortly, C_5 and lighter hydrocarbons are back flushed and are co-eluted in the C_4 alcohol section of the chromatogram. When the valve BACKFLUSH is switched too late, the ether component (MTBE, ETBE, or TAME) is vented fully or partially, resulting in an incorrect ether measurement.

9.1.3.4 DIPE may require a slightly shorter BACKFLUSH time than the other ethers. The system may require re-optimization if the analysis of DIPE is required.

9.1.3.5 To expedite BACKFLUSH time setting, the column vent in Fig. 2 can be connected to a second detector (TCD or FID), as described in Test M and used to set BACKFLUSH time based on oxygenates standard containing the ethers of interest.

9.2 Standardization

9.2.1 Determination of Retention time of each components by injecting known concentrations and by comparing RT (relative retention time) with those provided in Table 1.

9.2.2 Run the calibration standards (as mentioned in **8.1**) and establish the calibration curve for each oxygenate. Plot the response ratio (rsp_i).

$$rsp_i = (A_i / A_s)$$

where

A_i = area of oxygenate; and

A_s = area of internal standard.

as the y-axis versus the amount ratio (amt_i):

$$amt_i = (W_i / W_s)$$

where

W_i = mass of oxygenate, and

W_s = mass of internal standard

as the x-axis calibration curves for each oxygenate.

Check the correlation r^2 value for each oxygenate calibration.

The r^2 value should be at least 0.99 or better. r^2 is calculated as follows:

$$r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)}$$

where

$x = X_i - \bar{x}$

$y = Y_i - \bar{y}$

$X_i = amt_i$ ratio data point,

X = average values for all (amt_i) data points,

Y_i = corresponding rsp_i ratio data point; and

$\bar{y}$ = average values for all (rsp_i) data points.

9.2.3 Table 3 gives an example of r^2 calculation for an ideal data set of X_i and Y_i.

TABLE 3 Calculation of Correlation Coefficient-Example

SI. No.	X_i	Y_i	$x = X_i - \bar{x}$	$y = Y_i - \bar{y}$	xy	x^2	y^2
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
i)	1.0	0.5	-2.0	-1.0	2.0	4.0	1.0
ii)	2.0	1.0	-1.0	-0.5	0.5	1.0	0.25
iii)	3.0	1.5	0.0	0.0	0.0	0.0	0.0
iv)	4.0	2.0	+1.0	0.5	0.5	1.0	0.25
v)	5.0	2.5	+2.0	1.0	2.0	4.0	1.0
	$\bar{x}=3.0$	$\bar{y}=1.5$			Σxy	Σx^2	Σy^2
	$r^2 = \Sigma \dfrac{(xy)^2}{(\Sigma x^2)(\Sigma y^2)} = \dfrac{25.0}{(10.0)(2.5)} = 1.0$						

9.2.4 For each oxygenate i calibration data set, obtain the linear least-squares fit equation in the form

$$(rsp_i) = (m_i)\,(amt_i) + b_i$$

where

(rsp_i) = response ratio for oxygenate i (y-axis),

m_i = slope of linear equation for oxygenate i,

amt_i = amount ratio for oxygenate i (x-axis),

b_i = y-axis intercept.

9.2.5 The values m_i and b_i are calculated as follows

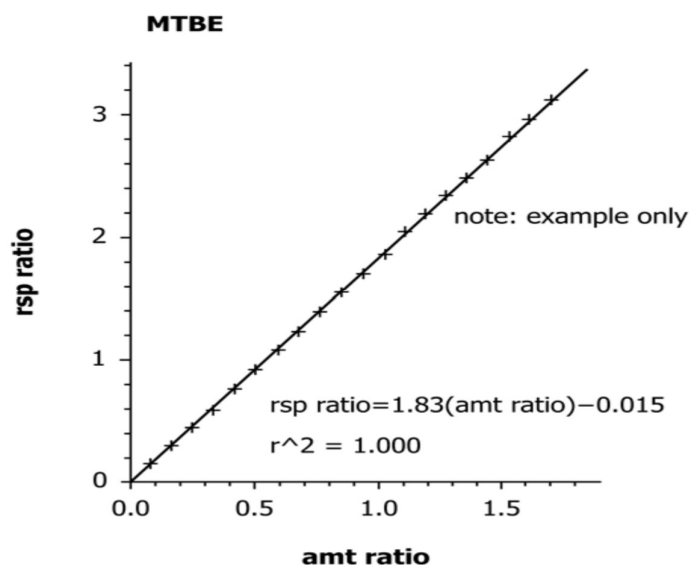$$m_i = \Sigma xy / \Sigma x^2$$

MTBE

FIG. 3 LEAST-SQUARES FIT CALIBRATION FOR MTBE

For the example in Table 3

$$m_i = \Sigma xy \,/\, \Sigma x^2 = 5/10 = 0.5$$

$$b_i = \bar{y} - m_i \, \bar{x} = 1.5 - (0.5)\,(3) = 0$$

Therefore, the least-squares fit (*see* Equation 6) for the above example in Table 3 is

$$(rsp_i) = 0.5 \,(amt_i) + 0$$

NOTE — Generally the b_i value may be either positive or negative, not be zero.

Fig. 3 gives an example of linear least-squares fit for MTBE and the resultant equation according to equation given in **9.2.4.**

9.2.6 For an optimum calibration, the absolute value of the y-intercept b_i must be at a minimum. In this case, A_i approaches zero when w_i is less than or equal to 0.1 mass percent. The equation is to determine the mass percent oxygenate i or w_i, reduces to equation given below.

The y-intercept can be calculated as given below.

$$w_i = (b_i/\,m_i)\,(w_s\,/\,w_g)\,100 \text{ percent}$$

where

w_i = mass percent oxygenate i, where wi is ≤ 0.1 mass percent,

W_s = mass of internal standard added to the gasoline samples, g and;

W_g = mass of gasoline samples, g.

NOTE — W_s and W_g vary slightly from sample to sample, so use average values.

9.2.7 Example: the calculation for the y-intercept (b_i) test using Fig. 3 for oxygenate i (MTBE), where b_i = 0.015 and m_i = 1.83. From 9.1, a typical sample preparation may contain approximately W_s = 0.4 g (0.5 ml) of internal standard and approximately W_g = 7 g (9.5 ml) of a gasoline sample. Substituting these values into equation 12 yields

$$w_i = (0.015/1.83)\ (0.4\ g\ /\ 7\ g)\ 100\ \text{percent}$$

$$= 0.05\ \text{mass percent}$$

9.2.8 Since w_i is less than 0.1 mass percent, the y-intercept b_i has an acceptable value for MTBE. Similarly, determine wi for all other oxygenates. For all oxygenates, w_i must be less than or equal to 0.1 mass percent. If any of the w_i values are greater than 0.1 mass percent, rerun the calibration procedure for oxygenate i or check instrument parameters and hardware or check for hydrocarbon interferences.

9.3 Quality Control

Before use, run a blank (diluents used in **8.4**) and any mid-range internal standard (Internal Quality Check Samples) on the prepared calibration line. The observed results shall remain within the precision of this method. In case large deviations are observed or desired precision is not met, recalibrate the instrument again.

10 PROCEDURE

10.1 Sample Preparation

Take 10 ml volumetric flask and tare it, then add 0.5 ml of internal standard (W_s) using a volumetric pipette and cap it. Record the net weight to nearest 0.1 mg and re-tare the capped flask. Fill the 10 ml volumetric flask to volume with sample, cap, and record the net mass (W_g) to the nearest 0.1 mg. Mix thoroughly and inject into the gas chromatograph. In case of an auto sampler, transfer an aliquot of the solution into a glass GC vial. Seal the GC vial with a TFE-fluorocarbon-lined septum.

> NOTE — If the sample is not immediately analyzed, store below 5 °C (40 °F). Recording and integrating devices shall be switched on to synchronize with sample injection.

10.2 Chromatographic Analysis

Inject prepared aliquot of the sample (as **10.1**), containing internal standard, into the gas chromatograph, using the same application and sample size as used for the calibration. An injection volume of 1.0 μL to 3.0 μL with a 15:1 split ratio has been practiced successfully. Obtain a chromatogram with integrated peak report presenting the retention times and integrated area of each detected component.

10.3 Chromatogram Elucidation

Compare the retention times and area of sample components with calibration analysis for identification and quantification of oxygenates present.

10.4 Calculation

10.4.1 *Oxygenates by Mass Percent*

Measure the area of each identified oxygenate peak and that of the internal standard. By using the least squares fit calibrations, as described in the MTBE example in Fig.3, calculate the mass of each oxygenate (W_i) in the gasoline samples, using the response ratio (rsp_i) of the areas of the oxygenate to that of the internal standard as follows:

$$(rsp_i) = (m_i)(amt_i) + b_i$$

where

m_i = slope of the linear fit,

b_i = y-intercept; and

amt_i = amount ratio as defined by equation given in **9.2.2**

Or $amt_i = (W_i/W_s) = (rsp_i - b_i) / m_i$

Or $W_i = [(rsp_i - b_i) / m_i] \ W_s$

$$= [(A_i/A_s - b_i) / m_i] \ W_s$$

To obtain mass percent (wi) results for each oxygenate

$$W_i = W_i \ (100) / W_g$$

where

W_g = weight of gasoline sample.

10.4.2 *Oxygenates by Volume Percent* — volumetric concentration of each oxygenate can be calculated as given below, if required.

$$V_i = w_i \ (D_f/D_i)$$

where

w_i = mass percent of each oxygenate,

v_i = volume percent of each oxygenate to be determined,

D_i = density at 15.0 °C of the individual oxygenate, as found in Table 1; and

D_f = density of the fuel at 15.0 °C, as determined by test method given in IS 1448 (Part 16)

10.4.3 *Oxygen by mass percent*

Use following equation to calculate the oxygen content of gasoline. Convert and sum the oxygen contents of all oxygenates accordance with equation 20 or 21.

$$W_{tot} = \Sigma \, (w_i \times 16.0 \times N_i)/M_i$$

Or $\quad\quad W_{tot} = (w_1 \times 16.0 \times N_1)/M1 + (w_2 \times 16.0 \times N_2)/M_2 + \dots$

where

w_i = mass percent of each oxygenate, as determined using equation given in 9.2.6,

w_{tot} = total mass percent oxygen in the fuel,

M_i = molecular mass of the oxygenate, as given in Table 1,

16.0 = atomic mass of oxygen,

N_i = number of oxygen atoms in the oxygenate molecule.

11 EXPRESSION OF RESULTS

11.1 Report the mass percent of each oxygenate to the nearest 0.01 mass percent. For concentrations less than or equal to 0.20 mass percent, report as "not detected."

11.2 Report the volume percent of each oxygenate to the nearest 0.01 volume percent. Report volume percent corresponding to less than or equal to 0.2 mass percent as "not detected".

11.3 Report the total mass percent of oxygen in the fuel to the nearest 0.01 mass percent.

12 PRECISION

The following precision data is applicable while using Helium as carrier Gas.

12.1 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would be in the normal and correct operation of the test method, exceed the value given in table 4 only in one case of twenty.

Table 4
(*Clause 12.1*)

Sl No.	Oxygenates in Gasoline	
	Component	Repeatability
(1)	(2)	(3)
i)	Methanol	$0.09 \, X^{0.59}$

ii)	Ethanol	$0.06 X^{0.61}$
iii)	Isopropanol	$0.04 X^{0.56}$
iv)	tertiary Butanol	$0.04 X^{0.56}$
v)	*n*-Propanol	$0.003 X^{0.57}$
vi)	MTBE	$0.05 X^{0.56}$
vii)	*sec*-Butanol	$0.003 X^{0.61}$
viii)	*di*-Isopropyl Ether	$0.08 X^{0.56}$
ix)	Isobutanol	$0.08 X^{0.56}$
x)	ETBE	$0.05 X^{0.82}$
xi)	tertiary-Pentanol	$0.04 X^{0.61}$

X= Mean result of the component in percent by mass

12.2 Reproducibility

The difference between two test results independently obtained by different operators working in different laboratories on nominally identical test material would be in the normal and correct operation of the test method, exceed the value given in Table 5 only in one case of twenty.

Table 5
(*Clause 12.2*)

Sl No.	Oxygenates in Gasoline	
	Component	Repeatability
(1)	**(2)**	**(3)**
i)	Methanol	$0.37 X^{0.61}$
ii)	Ethanol	$0.23 X^{0.57}$
iii)	Isopropanol	$0.42 X^{0.67}$
iv)	tertiary Butanol	$0.19 X^{0.67}$
v)	*n*-Propanol	$0.11 X^{0.57}$
vi)	MTBE	$0.12 X^{0.67}$
vii)	*sec*-Butanol	$0.44 X^{0.67}$
viii)	*di*-Isopropyl Ether	$0.42 X^{0.67}$
ix)	Isobutanol	$0.42 X^{0.67}$
x)	ETBE	$0.36 X^{0.76}$
xi)	tertiary-Pentanol	$0.15 X^{0.57}$

X= Mean result of the component in percent by mass.

ANNEX A
(*Clause 1.3 Note*)

HYDROCARBON INTERFERENCE

The following chromatogram depicts interference from hydrocarbons, which contain 10 percent by volume olefins in which 0.1 percent by volume of oxygenates are added. The chromatogram obtained is then compared with that of the sample in which no alcohol or ether.
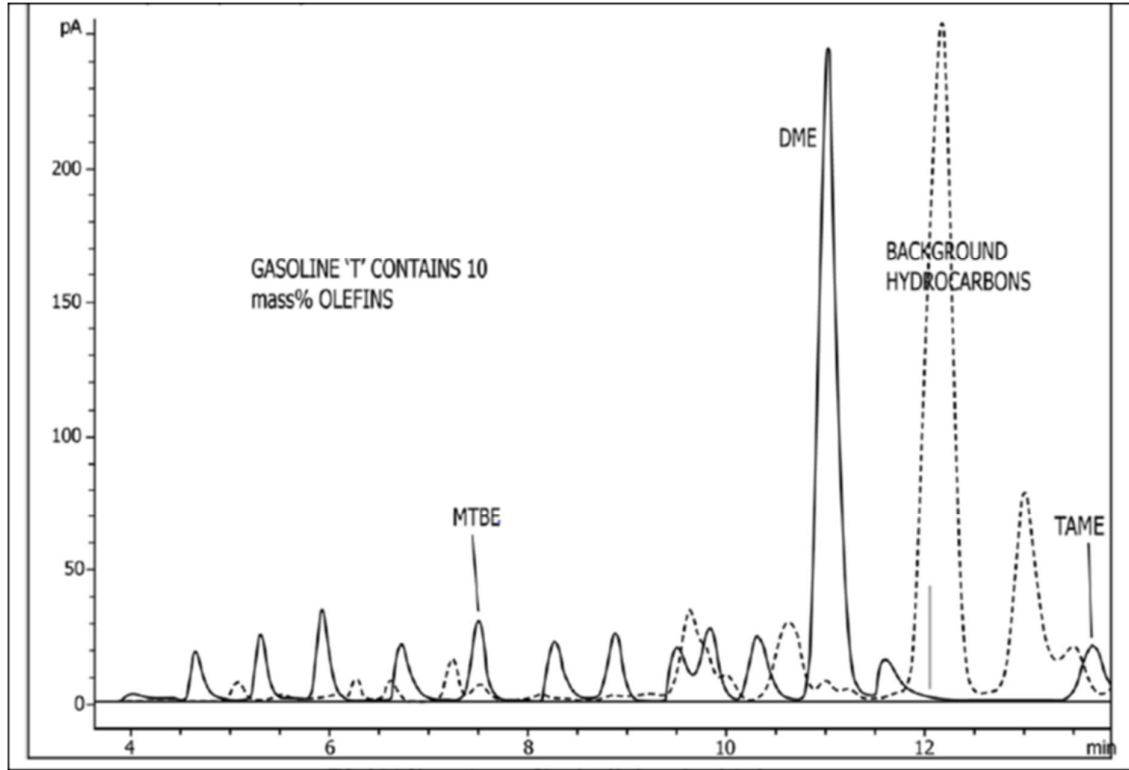

FIG. 4 CHROMATOGRAM DEPICTING HYDROCARBON INTERFERENCE