Final Draft from Technical Committee

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NEPAL STANDARD

Anhydrous Ethanol for Use as Blending Component in Motor Gasoline — Specification

Government of Nepal

Ministry of Industry, Commerce and Supplies

Nepal Bureau of Standards and Metrology (NBSM)

Kathmandu, Nepal

www.nbsm.gov.np

1 SCOPE

This standard specifies requirements, methods of sampling and test methods for anhydrous ethanol to be used as blending component with gasoline for automotive fuel in positive ignition engine vehicles.

2 REFERENCES

The following standards contain provisions, which through reference in this text constitute the provisions of the standards. 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 standard indicated below.

NS No.	*Title*
NS 476:2061	Test Method and Sampling for Absolute Alcohol
ISO 3696:1987	Water for analytical laboratory use — Specification and test methods
ISO 20846 : 2019	Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method
ISO 16591 : 2010	Determination of sulphur content — Oxidative microcoulometry method
NS *** :	Table for alcoholometry by hydrometer method
ISO 760: 1978	Determination of water — Karl Fischer method (General method)
NS *** :	Alcohol Denaturants — Specification
NS***	Methods of Sampling of Petroleum and its Products -Part 1 Manual Sampling
NS 356:2052 part 1	Determination of Specific Gravity

3 TERMINOLOGY

3.1 Ethanol — Ethanol is a pure organic chemical, otherwise known as hydroxy-ethane, corresponding to the constitution CH_3CH_2OH and molecular formula C_2H_5OH.

3.2 Ethyl Alcohol (Absolute Alcohol) — Ethyl alcohol (absolute alcohol) is a clear, colourless, and homogeneous liquid, consisting essentially of ethanol containing not more than 0.5 percent by volume of water.

3.3 Anhydrous Ethanol — Anhydrous ethanol is essentially ethyl alcohol, which is minimum 99.5 percent purity and having a boiling point of 78.5 °C without any denaturant. In this standard anhydrous ethanol refers to the ethyl alcohol which is denatured, meant for use in automotive gasoline blending.

3.4 Denaturant — Denaturant is a substance, prescribed by law, completely miscible in ethyl alcohol and of such a character that while its addition makes the material or any aqueous dilution of it unpleasant and unwholesome for potable purposes, its presence does not render anhydrous ethanol, either as such or blended with gasoline, unsuitable for use in automobile engines. The denaturants cannot be removed from alcohol except by complex and costly process.

4 REQUIREMENTS

4.1 Description

Anhydrous ethanol for use in automotive gasoline fuel shall be a clear, colorless, and homogeneous liquid, free from any suspended matters.

4.2 Denaturant

The denaturant to be admixed with ethyl alcohol and the proportion in which it is to be used is specified in NS ***(**Alcohol Denaturants — Specification)**.

4.2.1 *Prohibited Denaturants*

Specific mention must be made of some materials that have extremely adverse effects on fuel stability, automotive engines and fuel systems. These materials shall not be used as denaturants, for anhydrous ethanol for use in automobile fuels, under any circumstances. They are, methanol, pyrroles, turpentine, ketones and tars (high- molecular weight pyrolysis products of fossil or non-fossil vegetable matter). Unless a denaturant, such as a higher aliphatic alcohol or ether, is known to have no adverse effect on a gasoline-ethanol blend or on automotive engines or fuel systems, it shall not be used.

4.2.2 Subject to the effect of the added denaturant, anhydrous ethanol shall comply with the requirements for general purposes prescribed for ethyl alcohol.

4.3 Acidity

The material shall be neutral or acidic in reaction to phenolphthalein and when tested as prescribed in Annex D. The acidity, other than due to dissolved carbon dioxide shall not exceed the value given in Table 1, SI No. viii).

4.4 The material shall also comply with the requirements given in Table 1 when tested in accordance with appropriate methods given in col **5** of Table 1.

5 PACKING AND MARKING

5.1 Packing

5.1.1 The material shall be packed in such containers and packages as agreed to between the purchaser and the vendor, subject to the provisions of law in force from time to time

5.1.2 All containers in which the material is packed shall be dry, clean, free from substances soluble in anhydrous ethanol, and leak-proof.

5.1.3 Necessary safeguards against the risk arising from the storage and handling of large volume of flammable liquids shall be provided and all due precautions shall be taken at all times to prevent accidents or explosions.

5.1.4 Except when they are opened for the purpose of cleaning and rendering them free from alcohol vapour, all empty tanks or other containers shall be kept securely closed unless they have been thoroughly cleansed and freed from alcohol vapour.

5.2 Marking

5.2.1 Each container shall be marked legibly and indelibly with the following information:

a) Name of the material;

b) Source of the material (1G/2G/OGF);

c) Manufacturer's name;

d) Volume of the contents, in litres;

e) Recognized trade-mark, if any;

f) Date of packing;

g) Only for automotive use;

h) Highly flammable;

j) Hazardous chemical and injurious to health; and

k) Any other statutory requirements.

5.2.2 NS Certification Marking

The product confirming to the requirements of this standard may be certified under the provisions of the *Nepal Standards (Certification Mark) Act*, 2037 and the rules and regulations framed thereunder. The product may be marked with the Standard Mark.

6 SAMPLING

Representative samples of the material shall be drawn as prescribed in NS ***(**Methods of Sampling of Petroleum and its Products -Part 1 Manual Sampling)**

7 TEST METHODS

7.1 Tests shall be conducted as prescribed in col 5 of Table 1.

7.2 Quality of Reagents

Unless specified otherwise, pure chemicals and distilled water (see ISO 3696) shall be employed in tests.

NOTE — "Pure chemicals" shall mean chemicals that do not contain impurities, which affect the results of analysis (Laboratory or Analytical Reagent grade).

Table 1 Requirements of Anhydrous Ethanol for Use as Blending component in Motor Gasoline

(Cl 4.3, 4.4 *and* 7.1)

Sl. No.	Characteristics	Requirements		Reference to the Test Method Annex/ ASTM
		1 G	2G/OGF	
(1)	(2)	(3)	(4)	(5)
i)	Appearance	Clear, bright, and free from any sediments	Clear, bright, and free from any sediments	Visual observation
ii)	Relative density at 15.6/15.6 °C, *Max.*	0.7961	0.7965	Annex A
iii)	Ethanol, percent, *v/v*, *Min*[1)]. (excluding denaturant)	99.5	98[1)]	Annex B[3)]/ ASTM D 5501
iv)	Methanol, percent, *v/v*, *Max.*	0.5	0.5	ASTM D 5501/ ASTM D 4815[3)]
v)	Higher saturated alcohols (C3-C5), percent, *v/v*, *Max.*	–	1.5	NS ***
vi)	Boiling point, °C, *Min.*	–	To report	ASTM D 1078
vii)	Residue on evaporation, percent by mass, *Max.*	0.005	0.005	Annex C
viii)	Acidity (as CH_3COOH), mg/kg, *Max.*	30	30	Annex D[3)]/ASTM D 7795/
ix)	Alkalinity, mg/kg, *Max.*	NIL	NIL	Annex D
x)	Aldehyde (as CH_3CHO) content, mg/l, *Max.*	60	60	Annex E
xi)	Electrical conductivity, µS/m, *Max.*	300	500	Annex F
xii)	Copper, mg/kg, *Max.*	0.1	0.1	Annex G[3)]
xiii)	*p*He	–	6.5 – 8.0	ASTM D6423
xiv)	Inorganic chloride, mg/kg, *Max.*	–	3.0	ASTM D7319[3)]
xv)	Sulfur content, mg/kg, *Max.*	10	10	ASTM D7039/ASTM D 5453[3)]
xvi)	Sulphate content, mg/kg *Max.*	–	4	ASTM D7318[3)]/D7319/ D7328
xvii)	Water content, percent *v/v*, *Max.*	To Report (Note 2)	0.3	ASTM D7923[3)]/ASTM E1064
xviii)	Hydrocarbons, percent *v/v*	–	To report	Annex H
xix)	Miscibility with water	Miscible	Miscible	Annex J

NOTES

[1)] *In case of 2G/OGF technology process, total alcohol content shall be minimum 99.5 percent, as per Annex B.*

[2)] *To be reported by 1G manufacturer during release of product.*

[3)] *In case of disputes, this method shall be the referee method.*

1G -1st Generation Ethanol

Bioethanol [1st Generation (1G) Ethanol] is produced from biological sources, such as sugar containing materials like sugar cane, sugar beet, sweet sorghum etc.; starch containing materials, such as corn, cassava, rotten potatoes, etc.; as well, and from damaged food grains like wheat, broken rice etc. which are unfit for human consumption. Food grains during surplus phase and algal feedstock and cultivation of sea weeds were identified as potential feedstock for ethanol production from 1G technology.

2G-2nd Generation Ethanol

Ethanol produced through cellulosic materials, such as bagasse, wood waste, agricultural and forestry residues or other renewable resources like industrial waste, and 'Advanced biofuels' that are produced from lignocellulosic feedstocks (that is, agricultural and forestry residues, for example, rice and wheat straw/corn cobs and stover, bagasse, woody biomass), non-food crops (that is, grasses, algae), or industrial waste and residue streams and having low CO2 emission or high GHG reduction and do not compete with food crops for land use are categorized as second generation (2G) ethanol

OGF-Off Gas Fermentation

The large volume of waste gas produced at industrial facilities, such as refineries cannot be stored or transported; rather it must be combusted to make power locally and emitted as carbon dioxide (CO2). These refinery off-gases formed often contain components, such as olefins, hydrogen, CO2, CO, hydrocarbons, H2S, etc. Ethanol production through fermentation of gas mixtures containing CO, CO2 and H2 has just started operating at commercial scale and process is known as Off Gas Fermentation (OGF).

ANNEX A

[*Table* 1, *Sl No* ii)]

DETERMINATION OF RELATIVE DENSITY

A-1 GENERAL

Two methods have been prescribed for determination of specific gravity in anhydrous ethanol for use as automotive fuel. Both the methods can be used for the determination of specific gravity on routine basis. However, in the event of any dispute, Method 2 shall be treated as a referee method.

A-2 METHOD 1 - SPECIFIC GRAVITY BOTTLE METHOD

Determine the specific gravity of anhydrous ethanol using NS 356

A-3 METHOD 2 - OSCILLATING SAMPLE TUBE METHOD – (DIGITAL DENSITOMETER)

A-3.1 Summary of Test Method

A small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

A-3.2 Apparatus

A-3.2.1 *Digital Density Analyzer* — Consisting of a U-shaped, oscillating sample tube and a system for electronic excitation, frequency counting, and display. The analyzer must accommodate the accurate measurement of the sample temperature during measurement or must control the sample temperature as described in **A-3.2.2**. The instrument shall be capable of meeting the precision requirements described in this test method.

A-3.2.2 *Circulating Constant-Temperature Bath,*— Optional capable of maintaining the temperature of the circulating liquid constant to ± 0.05 °C in the desired range. Temperature control can be maintained as part of the density analyzer instrument package.

A-3.2.3 *Syringes* — At least 2 ml in volume with a tip or an adapter tip that will fit the opening of the oscillating tube.

A-3.2.4 *Flow-Through or Pressure Adapter* — For use as an alternative means of introducing the sample into the density analyzer either by a pump or by vacuum.

A-3.2.5 *Thermometer* — Calibrated and graduated to 0.1 °C, and a thermometer holder that can be attached to the instrument for setting and observing the test temperature. In calibrating the thermometer, the ice point and bore connections should be estimated to the nearest 0.05 °C.

A-3.3 Reagents and Materials

A-3.3.1 *Purity of Water* — Water, redistilled, fleshly boiled and cooled reagent water for use as a primary calibration standard.

A-3.3.2 *Petroleum Naphtha* — For flushing viscous petroleum samples from the sample tube.

Warning — Extremely flammable.

A-3.3.3 *Acetone* — For flushing and drying the sample tube.

Warning — Extremely flammable.

A-3.3.4 *Dry Air* — for blowing the oscillator tube.

A-3.4 Preparation of Apparatus

Set up the density analyzer and constant temperature bath following the manufacturer's instructions. Adjust the bath or internal temperature control so that the desired test temperature is established and maintained in the sample compartment of the analyzer. Calibrate the instrument at the same temperature at which the density of the sample is to be measured.

CAUTION — Precise setting and control of the test temperature in the sample tube is extremely important. An error of 0.1 °C can result in a change in density of one in the fourth decimal.

A-3.5 Calibration of Apparatus

A-3.5.1 Calibrate the instrument when first set up and whenever the test temperature is changed. Thereafter, conduct calibration checks at weekly intervals during routine operation.

A-3.5.2 Initial calibration, or calibration after a change in test temperature, necessitates calculation of the values of the constants *A* and *B* from the periods of oscillation (*T*) observed when the sample cell contains air and redistilled, freshly boiled and cooled reagent water. Other calibrating materials, such as n-nonane, n-tridecane, cyclohexane, and n-hexadecane (for high temperature applications) can also be used as appropriate.

A-3.5.2.1 While monitoring the oscillator period, *T,* flush the sample tube with petroleum naphtha, followed with an acetone flush and dry with dry air. Contaminated or humid air can affect the calibration. When these conditions exist in the laboratory, pass the air used for calibration through a suitable purification and drying train. In addition, the inlet and outlet ports for the U-tube must be plugged during measurement of the calibration air to prevent ingress of moist air. **A-3.5.2.2** Allow the dry air in the U-tube to come to thermal equilibrium with the test temperature and record the *T*-value for air.

A-3.5.2.3 Introduce a small volume (about 0.7 ml) of redistilled, freshly-boiled and cooled reagent water into the sample tube from the bottom opening using a suitable syringe. The test portion must be homogeneous and free of even the smallest air or gas bubbles. The sample tube does not have to be completely full as long as the liquid meniscus is beyond the suspension point. Allow the display to reach a steady reading and record the *T*-value for water.

A-3.5.2.4 Calculate the density of air at the temperature of test using the following equation:

dm, g/ml = 0.001293[273.15/T] [P/760] ... (1)

where

T = temperature, K, and

P = barometric pressure, Torr.

A-3.5.2.5 Determine the density of water at the temperature of test by reference to Table 2.

A-3.5.2.6 Using the observed *T*-values and the reference values for water and air, calculate the values of the constants *A* and *B* using the following equations:

$$A = [T_w^2 - T_a^2]/[d_w - d_a] \quad ...(2)$$

$$B = T_a^2 - (A \times d_a) \quad ...(3)$$

where

T_w = observed period of oscillation for cell containing water,

T_a = observed period of oscillation for cell containing air,

d_W = density of water at test temperature, and

d_a = density of air at test temperature.

Alternatively, use *T* and *d* values for the other reference liquid, if one is used.

A-3.5.2.7 If the instrument is equipped to calculate density from the constants *A* and *B* and the observed *T*-value from the sample, then enter the constants in the instrument memory in accordance with the manufacturer's instructions.

A-3.5.2.8 Check the calibration and adjust, if needed by performing the routine calibration check described in **A-5.3**.

A-3.5.2.9 To calibrate the instrument to display relative density, that is, the density of the sample at a given temperature referred to the density of water at the same temperature, follow sections **A-3.5.2.1** through **A-3.5.2.7**, but substitute 1.000 for d_W in performing the calculations described in **A-3.5.2.6.**

A-3.5.3 Weekly calibration adjustments to constants, *A* and *B* can be made if required, without repeating the calculation procedure.

*NOTE — The need for a change in calibration is generally attributable to deposits in the sample tube that are not removed by the routine flushing procedure. Although this condition can be compensated for by adjusting **A** and B, it is good practice to clean the tube with warm chromic acid solution, whenever a major adjustment is required. Chromic acid solution is the most effective cleaning agent; however, surfactant cleaning fluids have also been used successfully.*

Warning — *Causes severe bums. A recognized carcinogen.*

A-3.5.3.1 Flush and dry the sample tube as described in **A-3.5.2.1** and allow the display to reach a steady reading. If the display does not exhibit the correct density for air at the temperature of test, repeat the cleaning procedure or adjust the value of constant *B* commencing with the last decimal place until the correct density is displayed.

A-3.5.3.2 If adjustment to constant *B* was necessary in **A-3.5.3.1** then continue the recalibration by introducing redistilled, freshly boiled and cooled reagent water into the sample tube as described in **A-3.5.2.3** and allow the display to reach a steady reading. If the instrument has been calibrated to display the density, adjust the reading to the correct value for water at the test temperature (*see* Table 2) by changing the value of constant *A,* commencing with the last decimal place. If the instrument has been calibrated to display the relative density, adjust the reading to the value 1.0000.

*NOTE — In applying this weekly calibration procedure, it can be found that more than one value each for **A** and B, differing in the fourth decimal place, will yield the correct density*

reading for the density of air and water. The setting chosen would then be dependent upon whether it was approached from a higher or lower value. The setting selected by this method could have the effect of altering the fourth place of the reading obtained for a sample.

A-3.5.4 Some analyzer models are designed to display the measured period of oscillation only (*T*-values) and their calibration requires the determination of an instrument constant *K,* which must be used to calculate the density or relative density from the observed data.

A-3.5.4.1 Flush and dry the sample tube as described in **A-3.5.2.1** and allow the display to reach a steady reading. Record the *T*-value for air.

A-3.5.4.2 Introduce redistilled, freshly boiled and cooled reagent water into the sample tube as described in **A-3.5.2.3**, allow the display to reach a steady reading and record the *T*-value for water.

A-3.5.4.3 Using the observed *T*-values and the reference values for water and air (**A-3.5.2.4** and **A-3.5.2.5**), calculate the instrument constant *K* using the following equations:

$$K = [1.0000 - d_a]/[\,T_w^2 - T_a^2\,] \qquad \text{....(4)}$$

where

T_w = observed period of oscillation for cell containing water,

T_a = observed period of oscillation for cell containing air, and

d_a = density of air at test temperature.

A-3.6 Procedure

A-3.6.1 Introduce a small amount (about 0.7 ml) of sample into the clean, dry sample-tube of the instrument using a suitable syringe.

A-3.6.2 The sample can also, be introduced by siphoning. Plug the external TFE-fluorocarbon capillary tube into the lower entry port of the sample tube. Immerse the other end of the capillary in the sample and apply suction to the upper entry port using a syringe or vacuum line until the sample tube is properly filled.

A-3.6.3 Turn on the illumination light and examine the sample tube carefully. Make sure that no bubbles are trapped in the tube, and that it is filled to just beyond the suspension point on the right-hand side. The sample must be homogeneous and free of even the smallest bubbles.

A-3.6.4 Turn the illumination light off immediately after sample introduction, because the heat generated can affect the measurement temperature.

A-3.6.5 After the instrument displays a steady reading to four significant figures for density and five for *T*-values, indicating that temperature equilibrium has been reached, record the density or *T*-value.

A-3.7 Calculation

A-3.7.1 *Calculating Density Analyzers*

The recorded is the final result, as relative density.

A-3.7.2 *Non-calculating Density Analyzers*

Using the observed *T*-value for the sample and the *T*-value for water and appropriate instrument constant, *K,* determined in **A-3.5.4.3**, calculate the density or relative density using Equation 5. Carry out all calculations to six significant figures and round the final results to four.

Relative density, t/t= 1 + $K\ (T_s^2 - T_w^2)$ ... (5)

where

T_W = observed period of oscillation for cell containing water,

T_S = observed period of oscillation for cell containing sample,

K = instrument constant, and

t = temperature of test, °C.

Table 2 Density of Water

(Clauses A-3.5.2.5 a*nd* A-3.5.3.2)

Temperature *°C*	**Density** *g/ml*
(1)	(2)
0.0	0.999990
3.0	0.999984
4.0	0.999972
5.0	0.999964
10.0	0.999899
15.0	0.999699
15.56	0.999612
16.0	0.998943
17.0	0.998774
18.0	0.998595
19.0	0.998404
20.0	0.998203
21.0	0.997991
22.0	0,997709
23.0	0.997537
24.0	0.997295
25.0	0.997043
26.0	0.996702
27.0	0.996511
28.0	0.99623 I
29.0	0.995943
30.0	0.995043
35.0	0.994029
37.7	0.993042
40.0	0.992212
45.0	0.990200
50.0	0.990030
55.0	0.985600
60.0	0.983191
65.0	0.980546
70.0	0.977759
75.0	0.974837
80.0	0.971705
85.0	0.966606
90.0	0.965305
100	0.958345

A-4 Ethanol content calculation using Table 1 of NS ***(**Tables for Alcoholometry by Hydrometer Method)**, followed by conversion to specific gravity by using Appendix B of NS 476

ANNEX B

[*Table* 1, *Sl No.* iii)]

DETERMINATION OF ETHANOL CONTENT

B-1 GENERAL

Two methods have been prescribed for determination of ethanol content in anhydrous ethanol for use as automotive fuel. Both the methods can be used for determination of ethanol content on routine basis. However, in the event of any dispute, Method 2 shall be treated as a referee method.

B-2 METHOD 1 - ALCOHOLOMETRIC METHOD USING HYDROMETER

Determine the ethanol content in the anhydrous ethanol using method given in NS ***(**Tables for Alcoholometry by Hydrometer Method)**, using alcohol meter and Table 1 of (NS ***(**Tables for Alcoholometry by Hydrometer Method)**. Report in percent by volume.

IS NS ***(**Tables for Alcoholometry by Hydrometer Method)**, is for rectified spirit and its applicability to anhydrous ethanol meeting this specification need to be assessed.

B-3 METHOD 2 - GAS CHROMATOGRAPHIC METHOD

B-3.1 General

B-3.1.1 This test method covers the determination of the ethanol content of denatured fuel ethanol by gas chromatography.

B -3.1.2 Water cannot be determined by this test method and shall be measured by a procedure as given in ISO 760 and the result used to correct the chromatographic values.

B-3.1.3 This test method is inappropriate for impurities that boil at temperatures higher than 225 °C or for impurities that cause poor or no response in a flame ionization detector, such as water.

B-3.2 Summary of Test Method

A representative aliquot of the fuel ethanol sample is introduced into a gas chromatography equipped with a methyl silicone bonded phase fused silica capillary column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The ethanol and methanol components are identified by comparing their retention, times to the ones identified by analyzing standards under identical conditions. The concentration of all components are determined in mass percent area by normalization of the peak areas.

B-3.3 Apparatus

B-3.3.1 *Gas Chromatography* – Capable of operating at the conditions listed in Table 3. A heated flash vaporizing injector designed to provide a linear sample spilt injection (for example, 200 : 1) is required for proper sample introduction. Carrier gas controls shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure control devices and gauges shall be designed to attain the linear velocity required in the column used. A hydrogen flame ionization detector with associated gas

controls and electronics, designed for optimum response with open tabular columns, is required.

B-3.3.2 *Sample Introduction* – Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 0.1 to 0.5 PI injections are suitable. It should be noted that inadequate splitter design, poor injection technique, and overloading the column can result in poor resolution. Avoid overloading, particularly of the ethanol peak and eliminate this condition during analysis.

B-3.3.3 *Column – This* test method utilizes a fused silica open tubular column with non-polar methyl silicone bonded (cross-linked) phase internal coating. Any column with equivalent or better chromatographic efficiency and selectivity to those described in **B-3.3.3.1** can be used.

B-3.3.3.1 Open tubular column with anon-polar methyl silicone bonded (cross-linked) phase internal coating, either 150 m by 0.25 mm with a 1.0 µm film thickness, or 100 m by 0.25 mm with a 0.5 µm film thickness is required.

B-3.3.4 *Electronic Data Acquisition System*

Any data acquisition and integration device used for quantification of these analyses must meet or exceed these minimum requirements:

a) Capacity for at least 80 peaks/analysis,

b) Normalized area percent calculation with response factors,

c) Identification of individual components based on retention time,

d) Noise and spike rejection capability,

e) Sampling rate for fast (<1 sP) peaks,

f) Positive and negative sloping baseline correction,

g) and broad peaks, and

h) Non-resolved peaks separated by perpendicular drop or tangential skimming as needed.

B-3.3.5 *Containers*

B-3.3.5.1 *Vial* – Glass, threaded neck, approximately 22 ml capacity, short style.

Table 3 Typical Operating Conditions

(Clauses B-3.3.1, B-3.6.3 *and* B-3.8.1)

Column Temperature Program		
Column length	100m	150m
Initial temperature	15 ºC	60 ºC
Initial hold time	12 min	15 min
Program rate	30 ºC/min	30 ºC/min
Final temperature	250 ºC	250 ºC
Final hold time	19 min	23 min

Injector		**Detector**	
Temperature	300 °C	Type	Flame ionization
Split ratio	200 : 1	Temperature	300 °C
Sample size	0.1 to 0.5 µl	Fuel gas	Hydrogen (~30ml/min)
		Oxidizing gas	Air (~300 ml/min)
		Make-up gas	Nitrogen (~30 ml/min)

Carrier Gas	
Type	Helium
Average linear velocity	21-24 cm/s

B-3.3.5.2 *Bottle cap* – Molded plastic with polyethylene conical liner.

B-3.3.5.3 Bottle *cap* – Molded plastic with tin-foil liner. Tin foil liners are preferred to other metal liners because they are better.

B-3.4 Reagents and Materials

B-3.4.1 *Carrier Gas* – Helium, with a minimum purity of 99.95 mol percent. Oxygen removal systems and gas purifiers should be used.

Warning — Helium, compressed gas under high pressure.

B-3.4.2 *Detector Gases* – Hydrogen, air and nitrogen. The minimum purity of the gases used should be 99.95 percent for the hydrogen and nitrogen. The air should be hydrocarbon-free grade. Gas purifiers are recommended for the detector gases.

a) **Warning** — Hydrogen, extremely inflammable gas under high pressure.

b) **Warning** — Air and nitrogen, compressed gases under pressure.

B-3.4.3 *Standards for Calibration and Identification,*

Standards of all components to be analyzed are required for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

B-3.4.3.1 *Ethanol*

a) **Warning** — Two grades of ethanol are available. Only absolute ethanol 99.5 percent, *Min* meets the requirement of this test method.

b) **Warning** — These materials are flammable and may be harmful or fatal, if ingested or inhaled.

B-3.4.3.2 *Methanol*

Warning — These materials are flammable and may be harmful or fatal, if ingested or inhaled.

B-3.4.3.3 *Heptane*

Warning — These materials are flammable and may be harmful or fatal, if ingested or inhaled.

B-3.5 Sampling

B-3.5.1 Denatured ethanol can be sampled into an open container since a vapor pressure of less than 21 kPa is expected.

B-3.5.2 Transfer an aliquot of the sample into a septum vial and seal. Obtain the test sample for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

B-3.6 Preparation of Apparatus

B-3.6.1 Install and condition column in accordance with manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. When leaks are found, tighten or replace fittings before proceeding.

B-3.6.2 Adjust the carrier gas flow rate so that the average linear gas velocity, at the initial temperature of the run, is between 21 and 24 cm/s, as determined by the following equation:

$$\mu = L/t_m \qquad ...(6)$$

where

μ = average linear gas velocity in cm/s,

L = column length in cm, and

t_m = retention time of methane.

Flow rate adjustment is made by raising or lowering the carrier gas pressure (head pressure) to the injector.

B-3.6.3 Adjust the operating conditions of the gas chromatography (*see* Table 3) and allow the system to equilibrate.

B-3.6.4 *Linearity*

The linearity of the gas chromatography system shall be established prior to the analysis of samples.

B-3.6.4.1 The split ratio used is dependent upon the split linearity characteristics of the particular injector and the sample capacity of the column. The capacity of a particular column for a sample component is proportional to the amount of liquid phase (loading or film thickness) and the ratio of the column temperature to the component boiling point (vapour pressure). Overloading of the column may cause loss of resolution for some components and since overloaded peaks are skewed, variance in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, be aware of any peaks that may appear front skewed, indicating column overload. Note the component size and avoid conditions leading to this problem during actual analysis.

B-3.6.4.2 Splitting injector linearity must be established to determine proper quantitative parameters and limits. Use a standard mixture of known mass percentages of ethanol, methanol and 10 to 20 pure hydrocarbons, covering the boiling range of this test method. The determined mass percent for such component shall match the gravimetric known concentration within ± 3 percent relative.

B-3.6.4.3 The linearity of the flame ionization detector (FID) should be checked. A plot of the peak areas versus ethanol concentration for prepared standards in the concentration range of interest should be linear. If the plot is not linear, either the split ratio shall be increased or the detector range must be made less sensitive.

B-3.7 Calibration and Standardization

B-3.7.1 *Identification*

Determine the retention time of ethanol and methanol. By injecting amounts of each, either separately or in known mixtures, in proportions expected in the final blend using n-heptane as the solvent.

B-3.7.2 *Calibration*

Typical mass relative response factors for the components of interest are found in Table 4. These response factors shall be determined by analyzing a standard that has been blended according to **B-3.7.2.1**. This standard is comprised of the proportions of ethanol and methanol expected in the sample using n-heptane in place of the denaturant. A typical standard blend would be 96 percent ethanol, 0.1 percent methanol and 3.9 percent n-heptane. Calculate the mass relative response factor according to **B-3.7.3**.

B-3.7.2.1 *Preparation of blend*

B-3.7.2.1.1 Pre-blending calculations

In order to make blends of components at specific levels, it is necessary to calculate beforehand the mass of each component required to achieve these levels. Calculate masses as follows:

$$W_N = \frac{A \times T}{100} \qquad \text{...(7)}$$

where

W_N = mass of component N to be added, g;

A = desired percentage in the final blend; and

T = desired mass of typical final blend, g.

B-3.7.2.1.2 Procedure

B-3.7.2.1.2.1 Examine the vial and cap to verify that a leak-free closure is obtained. The rim at the top of the vial should be smooth and flat and the cap should fit snugly.

B-3.7.2.1.2.2 Plastic caps with tin foil liners provide a good seal unless blend components react with the tin. Polyethylene-lined caps usually provide a good closure but are not to be used for aromatic hydrocarbons and similar compound since these materials will, with-time, diffuse through the liner.

B-3.7.2.1.2.3 Weigh the vial and cap to the nearest 0.1 mg. Remove cap and add the first component to the vial, being careful not to allow the component to contact the rim of the vial, which could produce losses. Place the cap on the vial and re-weigh to the nearest 0.1 mg. Repeat this procedure with each additional component always being careful not to allow the content of the vial to contact the cap. After all components have been added and the final weighing completed, thoroughly shake the vial to mix the solution.

B-3.7.2.1.3 Calculations

Calculate the mass percent composition as follows:

$$\text{N, mass percent} = \frac{W_N \times 100}{\sum(W_N + W_O + W_P, \ldots)} \quad \ldots(8)$$

where

W_N, W_o, W_P= mass of components N, O, *P,* etc, g.

B-3.7.3 *Calculation of Mass Relative Response Factor*

B-3.7.3.1 Calculate the response factor for each component on a mass (weight) basis as follows:

$R_M = M/A$ ...(9)

where

R_M = mass (weight) response factor for a specific component g/unit;

M = mass (weight) of a specific component in the blend, g; and

A = area or peak height of the specific component peak, units.

B-3.7.3.1.1 Calculate the mass relative response factors as follows:

$PR_M\ (C_N) = R_M\ (C_N)/R_M\ (C_7)$ ...(10)

where

$PR_M\ (C_N)$ = mass (weight) relative response factor for a component, N, g/unit;

R_M (C_N)	=	mass (weight) response factor for specific component, N, determined in **B-3.7.3.1**, g/unit; and
R_M (C_7)	=	mass (weight) response factor for n-heptane, determined in **B-3.7.3.1**, g/unit.

NOTE — For purposes of this model calculation n-heptane has been chosen as the standard reference compound.

B-3.8 Gas Chromatographic Analysis Procedure

B-3.8.1 Set the instrument operating variables to the values specified in Table 3.

B-3.8.2 Set instrumental sensitivity such that any component of at least 0.002 mass percent can be detected and integrated.

B-3.8.3 Inject 0.1 to 0.5 µl of sample into the injection port and start the analysis. Obtain a chromatogram and peak integration report. A sample chromatogram is shown in Fig. 1.

B-3.8.4 The ethanol peak will require tangential skimming to be correctly integrated, if components of the denaturant elute on the ethanol peaks tail.

B-3.9 Calculation

B-3.9.1 Multiply the area of each identified peak by the appropriate mass relative response factor. Use those factors determined for individual compounds and use a factor of 1.000 for unknowns.

B-3.9.2 Determine the relative mass percent of the individual alcohols by using the following equation:

$$RM_i = \frac{AR_i \times 100}{AR_t} \qquad \ldots(11)$$

where

RM_i	=	relative mass percent of the individual alcohols,
AR_i	=	area of the individual alcohol peak corrected by the appropriate mass relative response factor (see B-3.8.1), and
AR_t	=	total area of all detected peaks corrected by their appropriate mass relative response factors (see B-3.8.1).

B-3.9.3 Obtain the mass percent of water in the sample. Test method ISO 760 or equivalent, can be used.

B-3.9.4 Determine the mass percent of the alcohols of interest by using the following equation:

$$M_i = \frac{RM_i \times (100 - \text{mass percent water in sample})}{100} \quad \ldots(12)$$

where

M_i = mass percent of the individual alcohol being determined, and

RM_i, = relative mass percent of the individual alcohol from **B-3.9.2**.

Table 4 Pertinent Physical Constants

(Clauses B-3.7.2 *and* B-3.9.5)

Component	Typical Mass Response Factors [1)]	Relative Density at 15.56 °C
(1)	(2)	(3)
Methanol	3.20	0.796
Ethanol	2.06	0.794
[1)] When n-heptane = 1.		

B-3.9.5 For the volumetric concentration of the alcohol, calculate as follows:

$$V_i = \frac{M_i \times D_s}{D_i} \quad \ldots \quad (13)$$

where

V_i = volume percent of component *i,*

M_i = mass percent of component, *i,* from **B-3.9.4**,

D_i = relative density at 15.56 °C (60 °F) of component, *i,* as found in Table 4, and

D_s = relative density of sample under study as determined in Annex A.

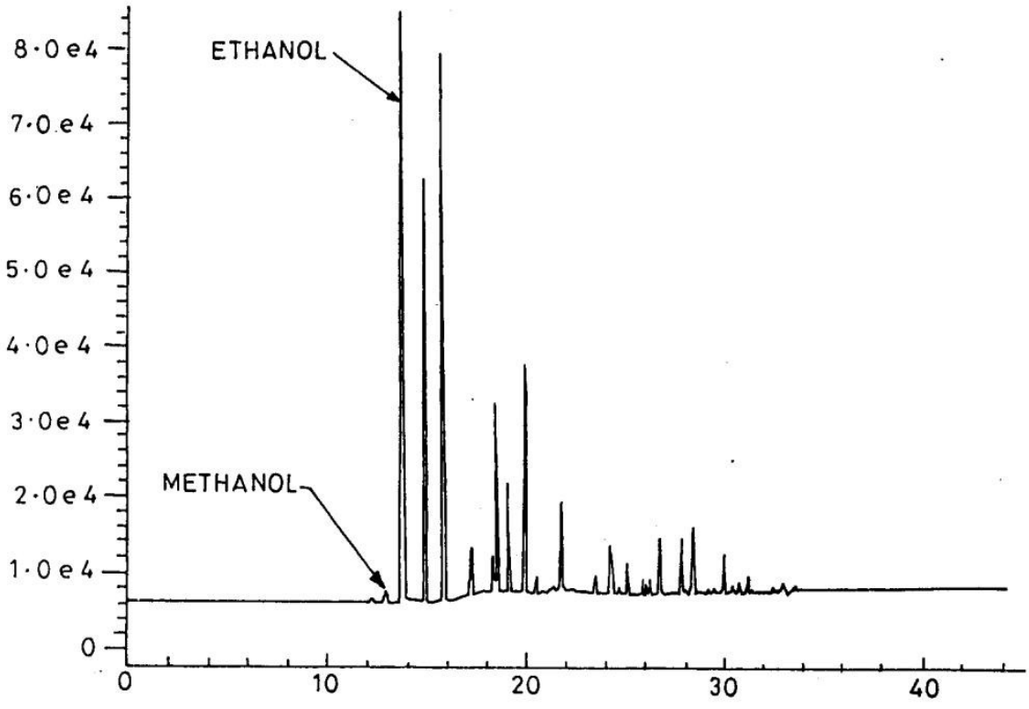


Fig. 1 Sample Chromatogram

ANNEX C

[*Table* 1, *Sl No.* (vii)]

DETERMINATION OF RESIDUE ON EVAPORATION

C-1 PROCEDURE

Evaporate on a water bath, 100 ml or more of the material to dryness in a weighed, clean, dry platinum, silica or resistance glass dish. Dry the residue for 30 min in an oven at a temperature of 100 ± 2°C. Cool in a desiccator and weigh.

C-2 CALCULATION

Residue on evaporation, percentage by mass

$$= \frac{(B - A) \times 100}{V \times S}$$

where

B = weight of dish after evaporation, drying, in g;

A = weight of empty dish, in g;

V = Volume of material taken for tests, in ml; and

S = Specific gravity of material determined at room temperature.

ANNEX D

[*Table* 1, *Sl No* (viii) *and* (ix)]

TEST FOR ALKALINITY AND DETERMINATION OF ACIDITY

D-1 GENERAL

D-1.1 Acidity

It is defined as a quality, state or degree of being acid. Very dilute aqueous solutions of low molecular weight organic acids (acetic acid) may be present in the anhydrous ethanol and are highly corrosive to many metals in vehicle operation when used as fuel or blending component with gasoline. It is therefore necessary to measure and keep such acids at a very low level in the anhydrous ethanol.

D-1.2 This test method estimates the amount of acid by titrating with alkali (NaOH) and report as acetic acid (CH_3COOH) mg/l.

D-2 REAGENTS

D-2.1 Standard Sodium Hydroxide Solution 0.l N

D-2.2 Phenolphthalein Indicator

Dissolve 0.5 g of phenolphthalein in 100 ml of anhydrous ethanol and carefully add standard sodium hydroxide solution till the colour is rendered faintly pink.

D-3 PROCEDURE

Place 100 ml of water and a few pieces of clean porous pot in a 500 ml conical flask of resistance glass, and boil gently for 5 min to eliminate carbon dioxide. Cool slightly and add 100 ml of the material. Boil gently for a further period of 5 min. At the end of this period, close the neck of the flask with a stopper carrying a soda-lime guard tube, and allow to cool. When cool, examine for alkalinity; if not alkaline, titrate with standard sodium hydroxide solution using a micro-burette.

D-4 CALCULATION AND REPORTING

D-4.1 Report whether the material is alkaline or acidic.

D-4.2 Calculate the acidity, if any, in terms of acetic acid and express it, in mg/l (as CH_3COOH) of the material taken for the test:

Acidity (as CH_3COOH), mg/1 = 600 *VN*

where

V = volume in ml, of standard sodium hydroxide solution required for the titration; and

N = normality of standard sodium hydroxide solution.

ANNEX E

[*Table* 1, *Sl No.* x)]

DETERMINTION OF ALDEHYDE CONTENT

E-1 METHODS

E-1.1 For Low Aldehyde Content

A suitable colour reaction is available when the aldehyde content (as CH_3CHO) is expected not to exceed 60 mg/1 of the material. This is based on the resinification that takes place and the yellow colour that results on treatment of acetaldehyde with sodium hydroxide. The procedure described under **E-4.1** provides a satisfactory qualitative limit test, but in case of dispute, the quantitative procedure described under **E-4.2** shall be adopted in the qualitative procedure, acetals are also included as aldehydes.

E-1.2 For Higher Aldehyde Content

For materials containing 0.05 to 0.5 percent of aldehydes, only the quantitative procedure described under **E-4.2** shall be adopted.

E-2 APPARATUS

E-2.1 Stoppered Flasks

Two, each of 250 ml capacity and identical in shape, size and colour.

E-3 REAGENTS

E-3.1 Sodium Hydroxide Solution

Dissolve 20 g of sodium hydroxide in water and dilute to 100 ml with water.

E-3.2 Stock Solution of Hydroxylamine Hydrochloride

Dissolve 20 g of hydroxylamine hydrochloride in 100 ml of water.

E-3.3 Meta-phenylenediamine Hydrochloride

E-3.4 Aldehyde Free Alcohol

Re-distil rectified spirit over solid caustic soda or caustic potash, add 2 to 3 g of meta-phenylenediamine hydrochloride per liter of rectified spirit, digest at ordinary temperature for several days or under a reflux condenser on a stream bath for several hours and distil slowly, rejecting the first 100 ml and the last 200 ml of the distillate.

E-3.5 Standard Sodium Hydroxide Solution, 0.1N

E-3.6 Bromophenol Blue Solution

Dissolve 0.1 g of bromophenol blue in 1.5 ml of standard sodium hydroxide solution of hydroxylamine hydrochloride with 100 ml of aldehyde-free alcohol, add 2 ml of bromophenol blue solution and then add standard sodium hydroxide solution till the characteristic dichroic yellowish green colour is obtained.

E-4 PROCEDURE

E-4.1 Qualitative Test

E-4.1.1 Mix 10 ml of the material with 5 ml of sodium hydroxide solution and set aside for 5 min.

E-4.1.2 The limit prescribed for aldehyde content (0.006 g/100 ml) shall be taken as not have exceeded, if no yellowish colour is produced in 5 min.

E-4.2 Quantitative Test

E-4.2.1 Take 50 ml of the material in a flask, add 25 ml of hydroxylamine reagent and 25 ml of distilled water. Allow to stand for 15 min. Meanwhile prepare a blank in a similar flask by using 25 ml of hydroxylamine reagent and 75 ml of distilled water. Titrate this solution with standard sodium hydroxide solution until the characteristic dichroic yellowish green colour appears. Titrate the sample solution with standard sodium hydroxide solution until the colour matches with that of the blank solution.

E-4.2.2 *Calculation*

Aldehyde content (as CH_3CHO), mg/1 = $880 \times (V - v) \times N$

where

V = volume of standard sodium hydroxide solution required for the titration, in ml;

v = volume of standard sodium hydroxide solution required, if any, in the blank, in ml; and

N = normality of standard sodium hydroxide solution.

ANNEX F

[*Table* 1, *Sl No.* (xi)]

DETERMINATION OF ELECTRICAL CONDUCTIVITY

F-1 GENERAL

This test method is applicable to field and routine laboratory measurements of the electrical conductivity using static samples. This test method utilizes dip-type or pipet-type conductivity cells for testing static samples. Temperature control and correction methods are also provided.

F-2 DETERMINATION OF CELL CONSTANT

F-2.1 For the purposes of this test method, the cell constant of the conductivity cell used shall be known within ±1 percent. The manufacturer's certification of the cell constant within this accuracy is generally considered satisfactory but the user is advised that damage could occur in shipment and it is best to re-check the cell constant when received. If the conductivity cell has been in service for a period subsequent to this certification, it shall be re-checked by the manufacturer, or in the laboratory.

F-2.2 Rinse the conductivity cell several times with water, then at least twice with the KCl reference solution that has conductivity nearest to that of the sample under test. Measure the resistance of the cell. Repeat the measurement on additional portions of the KCl reference solution until the value obtained remains constant.

F-2.3 For instruments reading measured conductance in Siemens, calculate the cell constant:

$J = 10^{-6} \times (K_1 + K_2/K_X)$

where

J = cell constant, cm^{-1};

K_1 = conductivity of the KCl in the reference solution at the temperature of measurement, µS/cm;

K_2= conductivity of the water used to prepare the reference solution, at the same temperature of measurement, µS/cm; and

K_X = measured resistance, ohm.

NOTE — Since the conductivities of a mixture of two solutions are not exactly additive, use of $K_1 + K_2$ is only an approximation and requires that K_2 be much smaller than K_1.

F-3 PROCEDURE

F-3.1 Precision Method Using Temperature Control

Use a dip-type or pipet-type cell. Rinse the cell, container, and thermometer thoroughly several times with water and then two or three times with the sample. Adjust the temperature to 15.6 ± 1°C. Allow sufficient time for equalization of temperatures. Read the conductance. Calculate conductivity according to **F-4** using Q = 1, since temperature correction is required.

F-3.2 Routine Method Using Temperature Correction

Use a dip-type or pipet-type cell. Rinse the conductivity cell thoroughly several times with water and then two or more times with the sample. Measure the resistance and the temperature (to the nearest 0.1°C), on successive portions of the sample until a constant value is obtained. If the measuring instrument is provided with a manual temperature compensator, adjust this to the sample temperature value before reading the instrument. If an automatic temperature compensator is provided, no adjustment is necessary, but sufficient time must be allowed to permit equalization of temperature. If instrument temperature compensation is used, calculate conductivity according to **F-4** using Q = l.

F-4 CALCULATION

For instruments reading measured conductance in Siemens, calculate the conductivity of the sample:

$$K = \frac{10^6 \times J \times K_X}{Q}$$

where

K = conductivity at 25 °C, µS/cm;

J = cell constant, cm-1;

K_X = measured resistance, ohm; and

Q = temperature correction factor.

ANNEX G

[*Table* 1, *Sl No.* (xii)]

DETERMINATION OF COPPER CONTENT IN ETHANOL

G-1 GENERAL

Copper is a very active catalyst for the low-temperature oxidation of hydrocarbons. Experimental work has shown that copper concentrations higher than 0.012 mg/kg in ethanol or ethanol blended gasoline can significantly increase the rate of gum formation. Hence, it is necessary to control and measure the copper presence in the anhydrous ethanol

Three methods have been prescribed for determination of copper content in anhydrous ethanol to be used in blending of automotive gasoline fuel. All the methods can be used for determination of copper content on routine basis. However, in the event of any dispute, Method 3 should be treated as a referee method.

G-2 METHOD 1 AND 2 - CHEMICAL METHODS

Determine the copper content of anhydrous ethanol using methods given in part 8 of NS 356.

G-3 METHOD 3 ATOMIC ABSORPTION METHOD

G -3.1 General

G-3.1.1 This test method covers the determination of copper by atomic absorption spectrophotometry. This test method is applicable in the range from 0.05 to 5 mg/1 of copper. The range may be extended to concentrations greater than 5 mg/l by dilution of the sample.

G-3.2 The sample shall be filtered through 0.45 µm membrane filler, if there is any suspended particle otherwise filtration is not necessary.

G-3.3 Summary of Test Method

Copper is determined by atomic absorption spectrophotometry. Copper sample is aspirated directly with no pretreatment.

G-3.4 Interferences

The lower concentration of the element as mentioned below:

Sodium, potassium, sulphate, and chloride (8000 mg/l each), calcium and magnesium (5000 mg/l each), nitrate (2000 mg/1), iron (1000 mg/1) and cadmium, lead, nickel, zinc, cobalt, manganese, and chromium (10 mg/l each) do not interfere in the analysis of copper.

NOTE — Instrument manufacturer's instructions for use of specific correction technique should be followed.

G-3.5 Apparatus

G-3.5.1 ***Atomic Absorption Spectrophotometer,*** for use at 324.7 nm.

NOTE — The manufacturer's instructions should be followed for all instrumental parameters. A wavelength other than 324.7 nm may be used if it has been determined to be equally suitable.

G-3.5.1.1 ***Copper Hollow-Cathode Lamp*** — Multi-element hollow-cathode lamps are available and have been found satisfactory.

G-3.5.2 ***Pressure-Reducing Valves*** — The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves which are operated manually or automatically through computer.

G-3.6 Reagents and Materials

G-3.6.1 ***Copper Solution, Stock*** (l.0 *ml* = 1.0 *mg* Cu)

Dissolve 1.000 g of electrolytic copper contained in a 250 ml beaker in a mixture of 15 ml of HNO_3 (sp gr 1.42) and 15 ml of water. Slowly add 4 ml of H_2SO_4 (1 + 1) and heat until SO_3 fumes evolve. Cool, wash down the beaker with water, and dilute to 1 litre with water or used commercially available SRM.

G-3.6.2 ***Copper Solutions Standard*** (1.0 ml = 0.1 mg Cu), dilute 100.0 ml of copper stock solution to 1 litre with ethanol.

G-3.6.3 ***Nitric Acid (sp gr 1.42), concentrated***

NOTE — If a high reagent blank is obtained, distill the $HN0_3$ or use a spectro grade acid.

G-3.6.4 *Oxidant*

G-3.6.4.1 *Air*

which has been passed through a suitable filter to remove oil, water, and other foreign substances, is the usual oxidant.

G-3.6.5 *Fuel*

G-3.6.5.1 *Acetylene,* standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 345 kPa.

CAUTION — 'Purified' grade acetylene containing a special proprietary solvent rather than acetone should not be used with polyvinyl chloride tubing as weakening of the tubing walls can cause potentially hazardous situation.

G-3.7 Standardization

G-3.7.1 Prepare 100 ml each of a blank and at least four standard solutions to bracket the expected copper concentration range of the samples to be analyzed by diluting the standard copper solution with ethanol. Prepare the standards each time the test is to be performed.

G-3.7.2 Aspirate the blank and standards and record the instrument readings.

G-3.7.3 Prepare an analytical curve by plotting on linear paper the absorbance *versus* standard concentration for each standard. Alternatively, read directly in concentration, if this capability is provided with the instrument.

G-3.8 Procedure

Aspirate each sample and determine its absorbance or Concentration at 324.7 nm.

G-3.9 Calculation

Calculate the concentration of copper in each sample, in milligrams per liter, using an analytical curve or alternatively, read directly in concentration (*see* **G-3.7.3)**.

ANNEX H

[*Table* 1, *Sl No.* xix)]

TEST METHOD FOR HYDROCARBON DETERMINATION IN FUEL ETHANOL BLENDS

H-1 One of the following test procedures can be utilized for hydrocarbon determination in ethanol.

H-2 METHOD A - STANDARD TEST METHOD FOR ETHANOL AND HYDROCARBON DETERMINATION IN FUEL ETHANOL AND GASOLINE BLENDS BY VOLUMETRIC TEST METHOD

H-2.1 Principle

This method is based on phase separation promoted by water (sodium chloride solution) addition to determinate the hydrocarbon (organic phase) content as the volume fraction. Other compounds, such as methanol, higher alcohols, ethers and other oxygenates, are miscible in the aqueous or organic phase and are quantified as ethanol or hydrocarbon content.

NOTE — Volume fraction of hydrocarbons is represented in percentage.

H-2.2 Reagents

H-2.2.1 *Sodium Chloride Solution* (*NaCl*)*,* 100 *g/l*

A solution prepared in accordance with the following or a commercially available sodium chloride solution with equivalent concentration. In order to prepare NaCl 100 g/l, transfer 100 g of NaCl to a 1000 ml volumetric flask, complete the volume to 1000 ml with water and homogenize the solution.

H-2.3 Apparatus

H-2.3.1 100 *ml Glass Measuring Cylinder with Stopper* — As shown in Fig. 2, calibrated at 3 points between 95 to 100 ml, and then full range as per the requirement.

NOTE —The measuring cylinder should be also calibrated at other points also, as required.

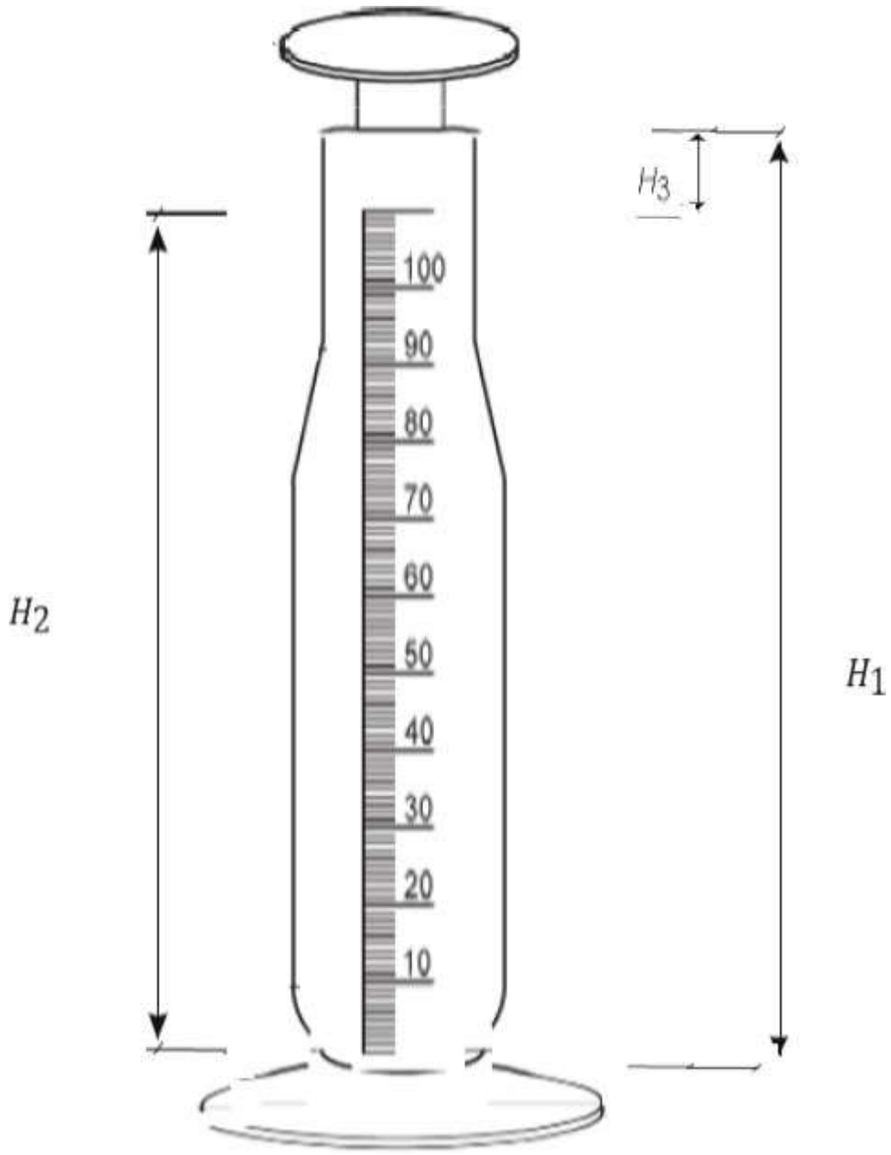
H-2.4 Procedure

H-2.4.1 The sample and the NaCl solution shall be at the room temperature.

H-2.4.2 Place 50 ml of the sample in the clean, defatted and dried measuring cylinder. Add the NaCl solution to complete the measuring cylinder to 100 ml. Place the stopper in the measuring cylinder. Turn the measuring cylinder slowly upside down ten times to extract the ethanol phase without forming an emulsion and preventing excessive pressure. Loosen the stopper to relieve the internal pressure of the measuring cylinder. Replace the stopper. Place the measuring cylinder on a leveled surface. Allow up to 10 min to permit complete separation of the aqueous and organic phase. Read the volume, in ml, of the organic phase by measuring the upper phase and subtracting the measure of the bottom phase. Read the lowest part of the both phases meniscus, as shown in Fig. 3. Record the organic phase volume to the nearest 0.5 ml.

H-2.5 Calculation

H-2.5.1 Calculate the hydrocarbon content in the sample using Table 5.



Where,

H_1 is the total high (maximum 260 mm);

H_2 is the internal height of the nominal range of indications (minimum 170 mm); and

H_3 is the distance between the upper scale and the top of the cylinder (minimum 35 mm).

Fig. 2 Measuring Cylinder Description

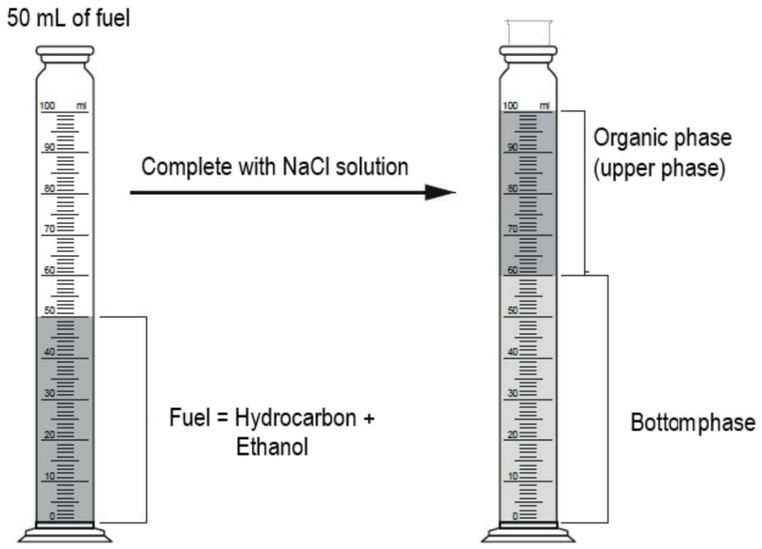


Fig. 3 Lecture Procedure of Upper and Bottom Phase

Table 5 Hydrocarbon Content in Fuel Sample
(Clause H-2.5.1)

***V*, ml**	***H*, percent**
Not detected [1)]	Not detected [1)]
< 0.5	< 2
≥ 0.5	(V × 2)

[1)]Record the hydrocarbon content as "not detected", if a volume of organic phase is not visually identified

where,

V = the volume of organic phase, in milliliters; and

H = the volume fraction of hydrocarbon content.

H-2.6 Report

Express the hydrocarbon content (V, percent) in Anhydrous Ethanol sample as integer number.

H-3 METHOD B — STANDARD TEST METHOD FOR HYDROCARBON DETERMINATION IN FUEL ETHANOL AND GASOLINE BLENDS BY USING GAS CHROMATOGRAPHY

H-3.1 General

H-3.1.1 This test method includes determination of paraffins, olefins, naphthenes, aromatics and unknowns (P.O.N.A.U.) in automotive gasolines and denatured ethanol using gas

chromatography and flame ionization detection (GC/FID). The samples having a boiling point more than 225 °C and components such as water cannot be determined.

H-3.1.2 The separation of individual hydrocarbons and oxygenated compounds may result in some peaks that represent coeluting components. Due to this possibility of coeluting peaks, caution is to be taken while interpreting the data.

NOTES

1 *Toluene and 2,3,3-trimethylpentane may coelute. If isooctane (2,2,4-trimethylpentane) and 2,3,4-trimethylpentane are present in the gasoline sample, it is probable that the sample contains 2,3,3-trimethylpentane. The concentration of 2,3,3-trimethylpentane is almost certain to be less than the concentration of 2,3,4-trimethylpentane. When determining the concentration of toluene and 2,3,3-trimethylpentane, it is essential that the gas chromatographic integrator has individual peak processing capabilities including peak expansion and perpendicular drop. To detect 2,3,3-trimethylpentane and toluene, it is essential for these components to be within a 5 : 1 ratio of each other with either component having the greater concentration. If these components are present in a greater than 5 : 1 ratio, toluene and 2,3,3-trimethylpentane may appear as a coeluted peak, thus causing the component in the smallest concentration to be integrated with the more concentrated component.*

2 *Components of automotive gasoline like toluene, 2-methylhexane, methylcyclopentane and n-hexane form coeluted peaks in this method.*

The number of coeluting peaks depends on the total number of individual components and olefinic components present in the sample. The possibility of coeluting components increases with the increase of components detected after n-octane.

H-3.2 Summary of Test Method

A sample is introduced into a gas chromatograph equipped with a fused silica, open tubular capillary column coated with a bonded methyl silicone liquid phase. The sample passes through the column and is separated into its individual components. The eluted components are detected using a flame ionization detector and recorded using an integrator or an integrating computer.

H-3.3 Apparatus

H-3.3.1 Gas Chromatograph

Any chromatographic instrument capable of the temperature program ranging from 0 °C to at least 300 °C. For sample introduction, the instrument should be equipped with a capillary inlet system designed to provide a linear split of the sample injected. A hydrogen flame ionization detector designed for capillary use is required.

H-3.3.2 Column

A fused silica, open tubular column, 100 m in length and 0.25 mm inside diameter, coated with a 0.5 μm thick film of bonded methyl silicone.

H-3.3.3 Signal Integrator

An electronic integrating device or computer capable of measuring peak areas and retention times. The integrating device shall be capable of processing a minimum of five hundred peaks using a corrected area normalization technique. The integrating device should be capable of measuring peaks eluting as fast as 0.04 s width at half height and have the capability of peak

processing parameters tailored to individual peaks. The electronic ranges of the integrating device shall be within the linear range of the detector/electrometer systems used. Common ranges are 1 V or 10 V.

H-3.3.4 Sample Introduction

Any method of sample introduction capable of delivering 0.1 to 0.5 µl to the split injector. Micro syringes, automatic liquid samplers, or valves may be used, if the injection produces a linear split of the sample.

H-3.4 Materials

H-3.4.1 Carrier Gas — Helium, 99.999 percent, pure.

H-3.4.2 Air — 99.999 percent, pure.

H-3.4.3 Hydrogen — 99.999 percent, pure.

NOTE — Hydrogen carrier may change the elution order of some components. Hydrogen carrier will require method optimization and demonstration of equivalency to helium carrier gas.

H-3.4.4 Make-up Gas (Helium or Nitrogen) m — 99.999 percent, pure.

H-3.4.5 Reference Standards — Hydrocarbons and oxygenated components of known purity.

H-3.5 Procedure

H-3.5.1 Preparation of Apparatus and Establishment of Conditions

Install the column in the gas chromatograph oven and condition the column according to the manufacturer's instructions. Adjust the gas chromatograph parameters as mentioned in Table6. These parameters will elute all components up to and including pentadecane (n C15).

Instrument parameters can be marginally changed to optimize for sample types and to optimize each gas chromatograph system.

H-3.5.2 Determine the carrier gas flow rate by injection of methane or natural gas. Calculate the linear gas velocity in cm/s using the following equation.

$$linear\ gas\ velocity = \frac{column\ length, cm}{retension\ time\ of\ methane, s}$$

A retention time of 6.51 min for methane at an oven temperature of 0°C, yielding a linear velocity of 25.6 cm/s, was found to be satisfactory.

H-3.5.3 Calculate and adjust the split ratio using the following equation.

$$split\ ratio = \frac{split\ vent\ \ flow\ rate \times coloumn\ \ flow\ rate}{coloumn\ \ flow\ rate}$$

H-3.5.4 Measure the volumetric flow rate at the column outlet. Alternatively, the volumetric flow rate through a capillary column can be calculated as follows.

$$F = \left[60\,\pi r^2\right]\left[T_{ref}\,/\,T\right]\left[2\left(p_i^3 - p_o^3\right)/\,3p_{ref}\left(p_i^2 - p_o^2\right)\bar{\mu}\right]$$

where

F = calculated column flow rate at standard temperature and pressure, in ml/min;

r= column radius, in cm;

p_i = inlet pressure (absolute), in dyne/cm^2;

p_o = outlet pressure (absolute), in dyne/cm^2;

P_{ref} = reference pressure, typically 1 atm (1.03 × 106 dyne/cm^2);

T = column temperature, in K;

T_{ref}= reference temperature, typically 298 K (25 °C);

$\bar{\mu}$ = average linear velocity, in cm/s; and

60 = to convert s to min.

Table 6 Recommended Instrument Parameters

(Clause H-3.5.1)

Detector type temperature, °C	Hydrogen flame ionization, 300
Inlet system type temperature, °C	Split 275
Column	
Length, m	100
Internal diameter, mm	0.25
Film thickness, µm	0.5
Stationary phase	Bonded methyl silicone
Temperature program	
Initial temperature, °C	0
Initial hold time, min	15
First program rate, °C/min	1
Final temperature, °C	50
Hold time, min	0
Second program rate, °C/min	2
Final temperature, °C	130
Hold time, min	0
Third program rate, °C/min	4
Final temperature, °C	270
Carrier gas	
Gas type	Helium
Linear velocity at 0°C, cm/s	25.6
Column head pressure, kPa (psi)	270 (35 to 50)
Split ratio	270:1
Sample size, µl	0.1 to 0.5
Total run time, min	142
NOTE — The use of constant flow is recommended.	

H-3.5.5 Make a blank baseline run to ensure that no stray peaks are detected and that the baseline signal at the upper temperature limit is steady and similar to that of the initial signal. The baseline rise at the end of the chromatographic temperature program should not exceed 1 percent of full scale. Further conditioning of the column may be required.

H-3.5.6 *Initial Evaluation and Performance of the Column*

H-3.5.6.1 The column shall meet the resolution requirements value for:

a) Benzene and 1-methyl-1-cyclopentene peaks. The resolution (R) value for these two peaks should have a value greater than 1.0.

b) *m*-Xylene and *p*-xylene peaks. The resolution (R) value for these two peaks should have a value greater than 0.40.

H-3.5.6.2 Calculate resolution (R) by using the following equation:

$$R = \frac{2\left(tR_2 - tR_1\right)}{1.699\ (Wh_2 + Wh_1)}$$

where

tR_1 = retention time of the first peak, seconds;

tR_2 = retention time of the second peak, seconds;

Wh_1 = peak width at half height for the first peak, seconds; and

Wh_2 = peak width at half height for the second peak, seconds.

NOTE — It is recommended that the resolution of the column be checked every 200 samples or a minimum of three times a year to assure column performance.

H-3.5.6.3 Measure the sensitivity of the system by analyzing a 100 mg/kg (0.010 mass percent) heptane standard. The heptane content measured should be 0.010 ± 0.002 mass percent.

H-3.5.6.4 Calculate the percent separation of m-xylene and p-xylene. Measure the distance from the valley between the two peaks to the apex of the m-xylene peak (a). Divide this value by the height of the m-xylene peak (b), and multiply by 100. The separation for gasoline is typically greater than 75 percent.

NOTE — The identification of components is based on retention times. To verify the system performance, it is recommended that the reference gasoline be run at six-month intervals, or when there is a change with the instrument. The purpose is to ensure that retention time drift has not resulted in misidentifications of the components and that the analytical system is continuing to produce accurate peak identifications.

H-3.5.6.5 A quality control (QC) sample shall be representative of samples being analyzed and run at regular intervals. The QC sample should contain oxygenated components at concentrations similar to the oxygenated components in the test samples. An interval of once per week or after every 15 samples is suggested. The quantitation results for benzene can be tracked by statistical quality control charts. Other components of interest in the reference

sample can be tracked in a similar manner. By monitoring these components over an extended period of time, the performance of the column and chromatographic system can be determined.

H-3.6 Identification and Standardization

H-3.6.1 *Identification*

Create a reference table similar to that of Table 7 by running the reference gasoline and/or calibration standards and adjusting the retention time or Kovats indices. Pay special attention to peak patterns as retention times for different columns, head pressure, etc., will vary from instrument to instrument.

H-3.6.2 It is recommended that the retention times for all oxygenated components be determined by analyzing calibration standards. Determine the retention times for ethanol and methanol by running concentrations expected in the test sample of both (either together or separately).

The split vent ratio may need to be adjusted in order to minimize ethanol peak tailing at high concentration but still be able to detect the ethanol peak at low concentration.

H-3.6.3 *Standardization*

H-3.6.3.1 The response factors for all components, except oxygenated components, are theoretical response factors and have been calculated using the following equation. All response factors may also be determined by analyzing standards.

$$F_i = \frac{\frac{\left[(C_{aw} \times C_n) + (H_{aw} \times H_n)\right]}{C_n} \times 0.7487}{C_{aw}}$$

where

Fi = relative response factor for a hydrocarbon type group of a particular carbon number;

Caw = relative atomic mass of carbon;

Cn = number of carbon atoms in the group;

Haw = relative atomic mass of hydrogen; and

Hn = number of hydrogen atoms in the group 0.7487 corrects the response of methane to unity.

In this case, methane will be considered to have a unity (1) response factor.

H-3.6.3.2 It is recommended that the response factors for all oxygenated components, other than ethanol and methanol, be determined by analyzing calibration standards.

H-3.6.3.3 The response factors for ethanol and methanol shall be determined by performing a single point calibration at concentrations dependent on the fuel being analyzed. The calibration standard methanol concentration (mass percent) for the response factor determination shall be within ± 20 percent of the test sample methanol concentration (mass percent).

H-3.6.3.4 The calibration standard ethanol concentration for the response factor determination when analyzing denatured ethanol (shall be in the range of 90 to 99 percent), preferably within ± 2 percent of the test sample ethanol concentration (mass percent).

H-3.6.3.5 The calibration standard ethanol concentration for the response factor determination when analyzing automotive ethanol fuel, E50-E85 shall be within ± 20 percent of the test sample ethanol concentration.

H-3.6.3.6 The calibration standard ethanol concentration for the response factor determination when analyzing oxygenated automotive gasoline containing ethanol, E1-E10, shall be within ± 20 percent of the test sample ethanol concentration, as given in Table 7.

Table 7 Suggested Calibration Standards for Ethanol and Methanol, in Mass Percent

(Clause H-3.6.1 *and* H-3.6.3.6)

Calibration Standard Methanol Concentration	Lowest Sample Methanol Concentration	Highest Sample Methanol Concentration
0.05	0.04	0.06
0.1	0.08	0.12
0.2	0.16	0.24
0.3	0.24	0.36
0.4	0.32	0.48
0.5	0.40	0.60
0.6	0.48	0.72
Calibration Standard Ethanol Concentration	**Lowest Sample Ethanol Concentration**	**Highest Sample Ethanol Concentration**
1	0.8	1.2
5	4	6
10	8	12
20	16	24
50	40	60
75	60	90
95	93	97

H-3.6.3.7 Prepare a standard containing ethanol and/or methanol, gravimetrically, at the concentration expected in the test sample and a known concentration of n-heptane using n-octane or iso-octane as the diluent. Correct for impurities and water content in the oxygenate stocks before preparing standards. Where available, certified reference materials may be used. Analyze the standard and calculate the RRF relative to n-heptane. Convert the RRF from relative to n-heptane to relative to methane using the factor 0.892. Methane will be considered to have a unity (1) response factor.

$$RF(n-heptane) = \frac{mass\ percent}{area}$$

$$RF(ethanol) = \frac{mass\ percent}{area}$$

$$RRF(ethanol) = \frac{RF(ethanol) \times 0.892}{RF\ (n-heptane)}$$

H-3.6.4 *Analysis*

H-3.6.4.1 Obtain a representative sample. Precaution should be taken wherever possible to minimize the loss of light ends from volatile samples in automotive gasolines. Obtain sample aliquot, prior to analysis. Cool the sample to less than + 4 °C prior to taking a sample aliquot or prior to filling autosampler vials. The sample aliquot or autosampler vial should be maintained at less than + 4 °C until ready for analysis or autosampler loading. The syringe can be cooled with the sample when using a manual injection technique.

H-3.6.4.2 Introduce a representative sample into the injection port and start the analysis. Obtain a chromatogram and a data report from the integrator. Retention times may differ because of slight variations in oven temperature and column flow rate. Retention times may also differ because of peak size, that is, column overload. Allow for differences in retention times of sample peaks with retention times of the reference peaks in the peak table. A computing integrator may be used for automatic peak identification; however, the chromatogram and report shall be carefully examined to ensure proper identification of the components.

H-3.6.4.3 When toluene and 2, 3, 3-trimethylpentane coelute and integration using perpendicular drop cannot be performed, the amount of each component may be estimated. The amount of 2, 3, 3-trimethylpentane can be estimated based on a fixed ratio to 2 ,3, 4-trimethylpentane. The ratio of 2, 3, 3-trimethylpentane to 2, 3, 4-trimethylpentane in alkylated gasoline is approximately 0.75. Analyze the sample as mentioned in **H-3.6.4.1**. Multiply the concentration of 2, 3, 4-trimethylpentane (mass, volume and mole percent) by 0.75 and subtract this amount from the toluene concentration. Alternatively, analyze the alkylate stream and experimentally determine the exact 2, 3, 4-trimethylpentane to 2, 3, 3-trimethylpentane ratio. Use the calculated ratio for the toluene correction. Subtract the amount of toluene determined from either of these methods from the coeluted toluene/ 2, 3, 3-trimethylpentane peak to obtain corrected values for these components. Report the concentration of toluene and 2, 3, 3-trimethylpentane as “corrected” and state the correction method.

H-3.6.5 *Calculation*

H-3.6.5.1 Calculate the normalized mass percentage of individual components using the following equation:

$$i,\ percent\ by\ mass = \frac{area\ (i) \times rf \times 100}{\sum [area(i) \times rf\,(i) \times area(k) \times rf\,(k) + ...]}$$

where,

area (i), area (j), area (k) = area of component i, j, k, etc.

rf (i), rf (j), rf (k) = mass relative response factor for components i, j, k, etc. determined experimentally for the component of interest

H-3.6.5.2 Calculate the normalized volume percentage of individual components using the following equation:

$$i, \text{ percent by volume} = \frac{\left(\frac{C_i}{D_i}\right) \times 100}{\sum\left[\left(\frac{C_i}{D_i}\right) + \left(\frac{C_k}{D_k}\right) + \ldots\right]}$$

where

C_i, C_j, C_k = percent by mass of components i, j, k, etc.; and

D_i, D_j, D_k = relative density of components i, j, k, etc., all determined at the same temperature.

H-3.6.5.3 Calculate the normalized mole percentage of individual components using the following equation:

$$i, \text{ percent by mole} = \frac{\left(\frac{C_i}{M_i}\right) \times 100}{\sum\left[\left(\frac{C_i}{M_i}\right) + \left(\frac{C_k}{M_k}\right) + \ldots\right]}$$

Where:

C_i, C_j, C_k = percent by mass of components i, j, k, etc.

M_i, M_j, M_k = relative molecular mass of components i, j, k, etc.

H-3.7 Report

Report the total concentration of paraffins, olefins, naphthenes, aromatics and unknowns on an absolute basis as percent by mass to two significant figures.

ANNEX J

[*Table* 1, *Sl No.* (xix)]

TEST FOR MISCIBILITY WITH WATER

J-1 PROCEDURE

J-1.1 Mix 10 ml of the material with 190 ml of water in a suitable glass vine and allow standing at ambient temperature for at least 10 min. Compare the clarity of the mixture with that of an equal volume of water.

J-1.2 The material shall be taken to comply with the specified requirement, if there is no noticeable difference in clarity between the mixture and water.

ANNEX K

ADDITIONAL/ALTERNATE TEST METHODS

Parameters	**Alternate Test Method**
Water content	ASTM E1064
Acidity	ASTM D 7795
pHe	ASTM D6423
Inorganic chloride	ASTM D7319/D7328
Copper	ASTM D1688-Method-A
Ethanol content	ASTM D 5501
Methanol content	ASTM D 5501
Sulfur	ASTM D2622, ASTM D3120, ASTM D7039,
Sulphate	ASTM D7318, ASTM D7319, ASTM D7328,