Designation: D 5797 – 96

An American National Standard

Standard Specification for Fuel Methanol M70-M85 for Automotive Spark-Ignition Engines[1]

This standard is issued under the fixed designation D 5797; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification covers a fuel blend, nominally 70 to 85 volume % methanol and 30 to 14 volume % hydrocarbons for use in ground vehicles with automotive spark-ignition engines. Appendix X1 discusses the significance of the properties specified. Appendix X2 presents the current status in the development of a luminosity test procedure for M70-M85.

1.2 The values stated in SI units are to be regarded as the standard. Values given in parentheses are provided for information only.

1.3 The following precautionary caveat pertains only to the test method portions–Annex A1, Annex A2, Annex A3, and Appendix X2 of this specification. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*[2]

2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products[3]
D 130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[3]
D 381 Test Method for Existent Gum in Fuels by Jet Evaporation[3]
D 512 Test Methods for Chloride Ion in Water[4]
D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)[3]
D 872 Test Method for Sulfonation Index of Road Tars[5]
D 1193 Specification for Reagent Water[4]
D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[3]
D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[6]
D 2622 Test Method for Sulfur in Petroleum Products by X-ray Spectrometry Method[7]
D 2988 Test Method for Water-Soluble Halide Ion in Halogenated Organic Solvents and Their Admixtures[8]
D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[7]
D 3231 Test Method for Phosphorus in Gasoline[7]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[7]
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[7]
D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[7]
D 4626 Practice for Calculation of Gas Chromatographic Response Factors[7]
D 4814 Specification for Automotive Spark-Ignition Engine Fuel[9]
D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[9]
D 4929 Test Methods for Determination of Organic Chloride Content in Crude Oil[9]
D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)[9]
D 5059 Test Method for Lead in Gasoline by X-ray Spectroscopy[9]
D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)[9]
D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)[9]
D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence[9]
E 203 Test Method for Water Using Karl Fischer Reagent[8]

[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is under the direct responsibility of Subcommittee D02.A on Gasoline and Oxygenated Fuels.

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[2] Reference to the following documents is to be the latest issue unless otherwise specified.

[3] *Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 04.03.

[6] *Annual Book of ASTM Standards*, Vol 06.04.

[7] *Annual Book of ASTM Standards*, Vol 05.02.

[8] *Annual Book of ASTM Standards*, Vol 15.05.

[9] *Annual Book of ASTM Standards*, Vol 05.03.

E 355 Practice for Gas Chromatography Terms and Relationships[10]

E 1145 Specification for Denatured Ethyl Alcohol, Formula 3A[8]

3. Terminology

3.1 *Definitions:*

3.1.1 *methanol*, *n*—methyl alcohol, the chemical compound CH_3OH.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aliphatic ether*—an oxygen-containing, ashless, organic compound in which the oxygen atom is interposed betweeen two carbon atoms (organic groups), has the general formula $C_nH_{2n+2}O$ with n being 5 to 8, and in which the carbon atoms are connected in open chains and not closed rings.

3.2.1.1 *Discussion*—Aliphatic compounds can be straight or branched chains and saturated or unsaturated. The term aliphatic ether, as used in this specification, refers only to the saturated compounds.

3.2.2 *fuel methanol (M70-M85)*—a blend of methanol and hydrocarbons of which the methanol portion is nominally 70 to 85 volume% .

3.2.3 *higher alcohols*—aliphatic alcohols of the general formula $C_nH_{2\ n+1}OH$ with *n* being 2 to 8.

3.2.4 *hydrocarbon*—those components in a methanol-hydrocarbon blend that contain only hydrogen and carbon.

4. Fuel Methanol M70-M85 Performance Requirements

4.1 Fuel methanol (M70-M85) shall conform to the requirements in Table 1.

NOTE 1—Most of the requirements cited in Table 1 are based on the best technical information currently available regarding the performance of these fuels in current technology vehicles. Requirements for sulfur, phosphorus, and lead are based on the use of gasoline defined in Specification D 4814 understanding that control of these elements will affect catalyst lifetime. The lead maximum is limited for Class 1 and Class 2 fuels to the lower limit of the test method. As greater experience is gained from field use of M70-M85 vehicles, and further vehicle hardware developments for the use of higher methanol content fuels occurs, it is expected that many of these requirements will change.

TABLE 1 Requirements for Fuel Methanol (M70-M85)

Properties	Class 1[A]	Class 2	Class 3
Methanol + higher alcohols, min, volume%	84	80	70
Hydrocarbon/aliphatic ether, volume%	14–16	14–20	14–30
Vapor pressure, kPa	48–62	62–83	83–103
(psi)	7.0–9.0	9.0–12.0	12.0–15.0
Lead, max, mg/L	2.6	2.6	3.9
Phosphorus, max, mg/L	0.2	0.3	0.4
Sulfur, max, mg/kg	160	200	300
	All Classes		
Higher alcohols (C_2–C_8), max, volume %		2	
Acidity, as acetic acid, max, mg/kg		50	
Solvent washed gum content, max, mg/100 mL		5	
Unwashed gum content, max, mg/100 mL		20	
Total chlorine as chlorides, max, mg/kg		2	
Inorganic chloride, max, mg/kg		1	
Water, max, mass%		0.5	
Appearance	This product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperatures unless otherwise agreed upon between the supplier and the purchaser.		

[A] See 4.1.1 for volatility class criteria.

4.1.1 Vapor pressure is varied for seasonal and climatic changes by providing three vapor pressure classes for M70-M85. The seasonal and geographic distribution for the three vapor pressure classes is shown in Table 2. Class 1 encompasses geographical areas with 6-h tenth-percentile minimum ambient temperature of greater than 5°C (41°F). Class 2 encompasses geographical areas with 6-h tenth-percentile minimum temperatures of greater than −5°C (23°F) but less than +5°C. Class 3 encompasses geographical areas with 6-h tenth-percentile minimum ambient temperature less than or equal to −5°C.

[10] *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 2 Seasonal and Geographical Volatility Specifications for Fuel Methanol (M70-M85)

NOTE 1—This schedule subject to agreement between the purchaser and the seller denotes the vapor pressure class of the fuel at the time and place of bulk delivery to fuel dispensing facilities for the end user. Shipments should anticipate this schedule.

State	January	February	March	April	May	June	July	August	September	October	November	December
Alabama	2	2	2	2	2/1	1	1	1	1	1/2	2	2
Alaska												
Southern Region	3	3	3	3	3/2	2/1	1	1/2	2/3	3	3	3
South Mainland	3	3	3	3	3/2	2/1	1/2	2	2/3	3	3	3
Arizona												
N of 34° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 34° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2
Arkansas	3	3	3/2	2/1	1	1	1	1	1/2	2	2/3	3
California[A]												
North Coast	2	2	2	2	2	2/1	1	1	1	1/2	2	2
South Coast	3/2	2	2	2	2/1	1	1	1	1	1/2	2/3	3
Southeast	3	3/2	2	2	2/1	1	1	1	1/2	2	2/3	3
Interior	2	2	2	2	2	2/1	1	1	1	1/2	2	2
Colorado												
E of 105° Longitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
W of 105° Longitude	3	3	3	3	3/2	2	2/1	1/2	2/3	3	3	3

TABLE 2 *Continued*

State	January	February	March	April	May	June	July	August	September	October	November	December
Connecticut	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Delaware	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
District of Columbia	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Florida												
N of 29° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2
S of 29° Latitude	2	2/1	1	1	1	1	1	1	1	1	1/2	2
Georgia	3	3/2	2	2/1	1	1	1	1	1	1/2	2	2/3
Hawaii	1	1	1	1	1	1	1	1	1	1	1	1
Idaho	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
Illinois												
N of 40° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 40° Latitude	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Indiana	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Iowa	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Kansas	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Kentucky	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Louisiana	2	2	2	2/1	1	1	1	1	1	1/2	2	2
Maine	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Maryland	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Massachusetts	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Michigan												
Lower Michigan	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Upper Michigan	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Minnesota	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Mississippi	2	2	2	2/1	1	1	1	1	1	1/2	2	2
Missouri	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Montana	3	3	3	3	3/2	2	2/1	1/2	2/3	3	3	3
Nebraska	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Nevada												
N of 38° Latitude	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
S of 38° Latitude	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
New Hampshire	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
New Jersey	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
New Mexico												
N of 34° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 34° Latitude	3	3	3/2	2/1	1	1	1	1	1	1/2	2/3	3
New York												
N of 42° Latitude	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
S of 42° Latitude	3	3	3	3/2	2/1	1	1	1	1/2	2	2/3	3
North Carolina	3	3	3/2	2	2/1	1	1	1	1/2	2/3	3	3
North Dakota	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Ohio	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Oklahoma	3	3	3	3/2	2/1	1	1	1	1/2	2	2/3	3
Oregon												
E of 122° Longitude	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
W of 122° Longitude	3	3/2	2	2	2	2/1	1	1	1/2	2	2	2/3
Pennsylvania												
N of 41° Latitude	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
S of 41° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Rhode Island	3	3	3	3/2	2/1	1	1	1	1/2	2	2/3	3
South Carolina	2	2	2	2/1	1	1	1	1	1	1/2	2	2
South Dakota	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Tennessee	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Texas												
N of 31° Latitude	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
S of 31° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2
Utah	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Vermont	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Virginia	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Washington												
E of 122° Longitude	3	3	3/2	2	2	2/1	1	1	1/2	2/3	3	3
W of 122° Longitude	3	3/2	2	2	2	2/1	1	1	1/2	2	2	2/3
West Virginia	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Wisconsin	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Wyoming	3	3	3	3	3/2	2	2/1	1/2	2	2/3	3	3

[A] Details of State Climatological Division by county as indicated:

California, North Coast—Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity

California, Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (except that portion lying east of Los Angeles County Aqueduct), Kings, Madera, Mariposa, Marced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada

California, South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct)

California, Southeast—Imperial, Riverside, San Bernadino, Los Angeles (that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct)

4.1.2 The hydrocarbons used shall have a final maximum boiling point of 225°C (437°F) by Test Method D 86, oxidation stability of 240-min minimum by Test Method D 525, and No. 1 maximum copper strip corrosion by Test Method D 130. The hydrocarbons may contain aliphatic ethers as blending components as are customarily used for automotive fuel.

4.1.3 Use of unprotected aluminum in fuel methanol (M70-M85) distribution and dispensing equipment will introduce insoluble aluminum compounds into the fuel causing plugged vehicle fuel filters. Furthermore, this effect can be exaggerated even with protected aluminum by elevated fuel conductivity caused by contact with a nitrile rubber dispensing hose. Therefore, unprotected aluminum and an unlined nitrile rubber dispensing hose should be avoided in fuel methanol (M70-M85) distribution and dispensing systems.[11]

5. Sampling

5.1 Sample in accordance with Practice D 4057, except that water displacement (10.3.1.8 of Practice D 4057) shall not be used.

5.2 Where practical, M70-M85 should be sampled in glass containers. If samples must be collected in metal containers, do not use soldered metal containers. This is because the soldering flux in the containers and lead in the solder can contaminate the sample. Plastic containers should be avoided.

5.3 A minimum sample size of about 1 L (1 qt) is recommended.

6. Test Methods

6.1 Determine the requirements enumerated in this specification in accordance with the following test methods:

NOTE 2—The appropriateness of ASTM test methods cited has not been demonstrated for use with M70-M85. In addition, test methods contained in the annexes and appendixes are in the developmental stages or lack precision and bias determinations.

6.1.1 *Methanol*—A procedure for a test method for methanol content of fuel methanol (M70-M85) is included as Annex A1. Verification of the appropriateness of this test method has indicated that the precision of this method may not be adequate. As work continues to develop a method, this procedure remains the best available.

6.1.2 *Hydrocarbon/Aliphatic Ether*—Use Test Method D 4815 to determine higher alcohols, methyl *tert*-butyl ether (MTBE), and other ethers. Water may also be determined if the gas chromatograph is equipped with a thermal conductivity detector. As an alternative, water can be determined by the Karl Fischer test method (see 6.1.9). The concentration of methanol, other alcohols, and water can be added, and the sum subtracted from 100 to get the percent of hydrocarbons/aliphatic ethers. An alternative test method is contained in Annex A2.

6.1.3 *Vapor Pressure*— Test Methods D 4953, D 5190, or D 5191.

6.1.4 *Acidity*—Test Method D 1613.

6.1.5 *Gum Content, Solvent Washed and Unwashed*—Test Method D 381.

6.1.6 *Total Chlorine as Chloride*—Test Methods D 4929, Method B.

6.1.7 *Lead*—Test Method D 5059. With Test Method D 5059, prepare the calibration standards using methanol (reagent grade) as the solvent to prevent errors caused by large differences in carbon-hydrogen ratios.

6.1.8 *Phosphorus*—Test Method D 3231.

6.1.9 *Water*—Test Method E 203.

6.1.10 *Sulfur*—Test Methods D 1266, D 2622, D 3120, or D 5453. With Test Method D 2622, prepare the calibration standards using methanol (reagent grade) as the solvent to prevent errors caused by large differences in carbon-hydrogen ratios.

6.1.11 *Inorganic Chloride*—Inorganic chloride can be determined by Test Methods D 512 (Method C) or D2988. Also, see the test method in Annex A3. Another test method is under development.

7. Keywords

7.1 acidity; alcohol; automotive spark-ignition engine fuel; chloride; copper corrosion; ether; fuel methanol (M70-M85) for automotive spark-ignition engines; gum content; solvent washed; hydrocarbon; inorganic chloride; lead; MTBE; M70-M85; methanol; oxidation stability; oxygenates; phosphorus; sulfur; total chlorine; vapor pressure; volatility; water

[11] American Automobile Manufacturers Association, "Fuel Methanol Compatibility Standards and Dispensing Equipment List for M85 Fueled Vehicles," October 1994.

ANNEXES

(Mandatory Information)

A1. TEST METHOD FOR DETERMINATION OF METHANOL IN FUEL METHANOL (M70-M85) FOR AUTOMOTIVE SPARK-IGNITION ENGINES

A1.1 Scope

A1.1.1 This test method covers a procedure for determination of methanol in fuel methanol (M70-M85) by gas chromatography. This test method is appropriate for fuels containing 70 to 95 volume % methanol.

A1.1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

A1.2 Referenced Documents

A1.2.1 *ASTM Standards*:

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[7]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[7]

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[7]

D 4626 Practice for Calculation of Gas Chromatographic Response Factors[7]

E 355 Practice for Gas Chromatography Terms and Relationships[10]

A1.3. Terminology

A1.3.1 *Definitions of Terms Specific to This Standard:*

A1.3.1.1 *low-volume connector*—special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Also referred to as a zero dead-volume union.

A1.3.1.2 *split ratio—in gas chromatography using capillary columns*—the ratio of the total flow of the carrier gas to the sample inlet versus the flow of carrier gas to the capillary column.

A1.3.1.3 *TCEP*—1,2,3-tris-2-cyanoethoxypropane. A gas chromatographic liquid phase.

A1.3.1.4 *WCOT*—abbreviation for a type of capillary column, wall-coated open tubular, used in gas chromatography. This type of column is prepared by coating the inside of the capillary with a thin film of stationary phase

A1.4 Summary of Test Method

A1.4.1 An internal standard, *tert*-amyl alcohol, is added to the sample that is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample passes into the first column, a polar TCEP column that elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

A1.4.2 After methylcyclopentane, but before methanol elutes from the polar column, the valve is switched to backflush the oxygenates onto a WCOT nonpolar column. The methanol and internal standard elute from the nonpolar column in boiling point order, before elution of any major hydrocarbon constituents.

A1.4.3 After the internal standard elutes from the non-polar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons. The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of methanol is calculated with reference to the internal standard.

A1.5 Significance and Use

A1.5.1 The production of fuel methanol (M70-M85) requires knowledge of the methanol content to ensure acceptable commercial fuel quality. The methanol content of fuel methanol (M70-M85) affects the performance of an automobile designed to run on such fuel.

A1.5.2 This test method is applicable to both quality control in the production of fuel methanol (M70-M85) and for the determination of fuel contamination.

A1.6 Apparatus

A1.6.1 *Chromatograph*— See Practice E 355 for specific descriptions and definitions.

A1.6.1.1 *Gas Chromatographic Instrument*, operable at the conditions given in Table A1.1 and having a column switching and backflushing system equivalent to Fig. A1.1. Carrier gas flow controllers must be designed for use at the required flow rates (see Table A1.1). Pressure control devices and gages must be designed for use at the pressures required. Table A1.2

A1.6.1.2 *Detector*, either a thermal conductivity detector (TCD) or flame ionization detector (FID) may be used. The system must have sufficient sensitivity and stability to sense absolute concentration changes of 0.01 volume % of methanol or internal standard at the 50 volume % level.

A1.6.1.3 *Switching and Backflushing Valve*, a ten-port valve, to be located within the gas chromatographic column oven, capable of performing the functions described in A1.10 and illustrated in Fig. A1.1. The valve must be of lowvolume

TABLE A1.1 Chromatographic Operating Conditions

	Temperatures, °C	Flows	mL/min
Column Oven	60	to injector	75
Injector	200	column	5
Detector		auxiliary	3
TCD	200	makeup	18
FID	250		
Valve	60		
Carrier Gas—Helium			
Sample size, µL		1	
Split ratio		15:1	
Backflush, min		0.2–0.3	
Valve reset time, min		8–10	
Total analysis time, min	18–20		

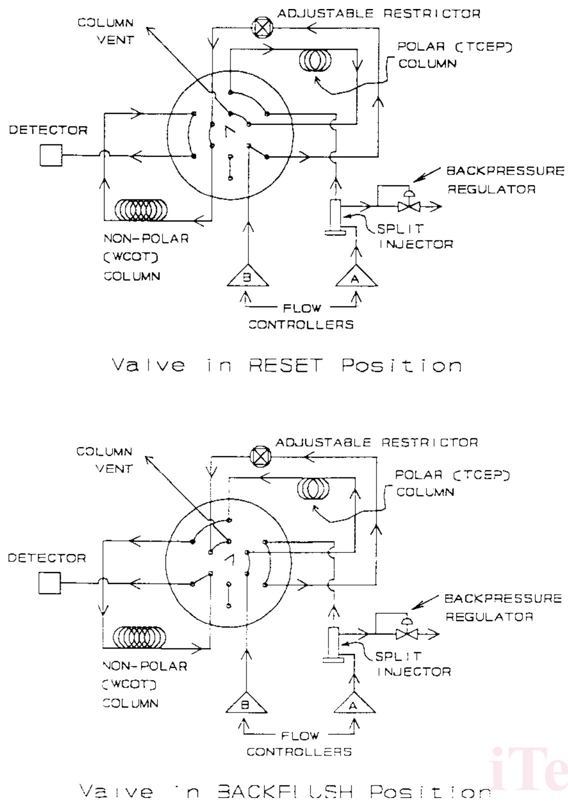

FIG. A1.1 Schematic of Chromatographic System

TABLE A1.2 Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table A1.1

Component	Retention Time, min	Relative Retention Time (*t*-Amyl Alcohol = 1.00)
Methanol	3.21	0.44
t-Amyl Alcohol	7.30	1.00

design and not contribute significantly to chromatographic deterioration.[12]

A1.6.1.4 *Automatic Valve Switching Device*, (strongly recommended to ensure repeatable switching times) a device synchronized with injection and data collection times. If no such device is available, a stopwatch, started at the time of injection, should be used to indicate the proper valve switching time.

A1.6.1.5 *Injection System*, a splitting-type inlet device. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

A1.6.1.6 *Sample Introduction System*, any system capable of introducing a representative sample into the split inlet device.

NOTE A1.1—Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully.

A1.6.2 *Data Presentation or Calculation System*:

A1.6.2.1 *Recorder*, a recording potentiometer or equivalent with a full-scale deflection of 1 mV or less, and full-scale response time of 1 s or less, with sufficient sensitivity and stability to meet the requirements of A1.6.1.2.

A1.6.2.2 *Integrator or Computer Devices*, capable of meeting the requirements of A1.6.1.2, and providing graphic and digital presentation of the chromatographic data. Peak heights or areas can be measured by computer, electronic integration, or manual techniques.

A1.6.3 *Columns*—Two columns are used as follows:

A1.6.3.1 *Polar Column*— Any column with equivalent or better chromatographic efficiency and selectivity to that described in A1.6.3.1(*a*) can be used. The column must perform at the same temperature as required for the column in A1.6.3.2. This column performs a pre-separation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the nonpolar column in A1.6.3.2.

(a) TCEP Micro-Packed Column,[13] 560-mm (22-in.) by 1.6-mm (1⁄16-in.) outside diameter by 0.38-mm (0.015-in.) inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20 % by mass TCEP on 80/100 mesh Chromosorb P(AW). This column is being used to develop precision and bias data for A1.15.

A1.6.3.2 *Nonpolar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in A1.6.3.2(*a*) and illustrated in Fig. A1.2 can be used.

(a) WCOT Methyl Silicone Column, 30-mm (1.181-in.) long by 0.53-mm (0.021-in.) inside diameter fused silica WCOT column with a 2.65-μm film thickness of crosslinked methyl siloxane. This column is being used to develop precision and bias data for A1.15.

A1.7 Reagents and Materials

A1.7.1 *Carrier Gas*, carrier gas appropriate to the type of detector used. The minimum purity of the carrier gas shall be 99.995 mol %.

NOTE A1.2—Helium has been used successfully.

A1.7.2 *Methanol, 99.9 % Purity*, required to establish identification by retention time and for calibration. Shall be of known purity and free of the other components to be analyzed. (**Warning—**See Note A1.3.)

NOTE A1.3—**Warning:** Flammable. Health hazard.

A1.7.3 *Methylene Chloride*, used for column preparation. Reagent grade, free of nonvolatile residue. (**Warning**—See Note A1.4).

NOTE A1.4—**Warning:** Health hazard.

A1.7.4 *Nitrogen, 99.998 mol %*, used to prepare tubing for the micro-packed TCEP column. (**Warning**—See Note A1.5).

NOTE A1.5—**Warning:** Gas under pressure.

A1.7.5 *Tert-Amyl Alcohol (2-Methyl-2-Butanol), 99 % Purity*, used as the internal standard. (**Warning**—See Note A1.6).

[12] A Valco Model No. CM-VSV-10-HT valve with 1.6-mm (1⁄16-in.) fittings has been found satisfactory for this purpose. This is the valve being used in the majority of the analyses for the development of the data for A1.15. A Valco Model No. C10W with 0.8-mm (1⁄31-in.) fittings is recommended for use with columns of 0.32-mm inside diameter and smaller.

[13] Available from Hewlett Packard Co., Wilmington, DE.