



Designation: D7754 – 23

Standard Test Method for Determination of Trace Oxygenates in Automotive Spark-Ignition Engine Fuel by Multidimensional Gas Chromatography¹

This standard is issued under the fixed designation D7754; 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 test method covers the determination of trace oxygenates in automotive spark-ignition engine fuel. The method used is a multidimensional gas chromatographic method using 1,2-dimethoxy ethane as the internal standard. The oxygenates that are analyzed are: methyl-tertiary butyl ether (MTBE), ethyl-tertiary butyl ether (ETBE), diisopropyl ether (DIPE), methanol, tertiary-amyl methyl ether (TAME), n-propanol, i-propanol, n-butanol, i-butanol, tert-butyl alcohol, sec-butyl alcohol, and tert-pentanol. Ethanol is usually not measured as a trace oxygenate since ethanol can be used as the main oxygenate compound in finished automotive spark-ignition fuels such as reformulated automotive spark-ignition fuels. The concentration range of the oxygenates covered in the ILS study was from 10 mg/kg to 2000 mg/kg. In addition this method is also suitable for the measurement of the C5 isomeric alcohols (2-methyl-1-butanol, 2-methyl-2-butanol) present from the fermentation of ethanol.

1.2 The ethanol blending concentration for which this test method applies ranges from 1 % to 15% by volume. Higher concentrations of ethanol coelute with methanol in the analytical column. Lower levels of ethanol, similar to the other oxygenate, can be calibrated and analyzed also. If higher ethanol concentrations are expected, the window cutting technique can be used to avoid ethanol from entering the analytical column and interfere with the determination of the other oxygenates of interest. Refer to [Appendix X1](#) for details.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3.1 Alternative units, in common usage, are also provided to increase clarity and aid the users of this test method.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography
- D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
- E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 Definitions:

3.1.1 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practice E355 or Terminology D4175, or both.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *electronic pressure control, n*—electronic pneumatic control of carrier gas flows. Can be flow or pressure programmed to speed up elution of components.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

3.2.2 *flame ionization detector (FID)*, *n*—detector used to analyze the components eluting from the column.

3.2.3 *fluidic switch*, *n*—device that reverses the directional flow in a union T altering the pressure at the midpoint. In its simplest design it is also known as a Dean Switch.

3.2.4 *inlet*, *n*—capillary split/splitless inlet system operated in the split mode is recommended. Operate the inlet within its linear range.

3.2.4.1 *split ratio*, *n*—*in capillary gas chromatography*, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column is expressed by:

$$\text{Split ratio} = (S + C)/C \quad (1)$$

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.2.5 *low volume connector*, *n*—special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.2.6 *multidimensional gas chromatography*, *n*—gas chromatographic technique where using hardware (valves, pressure switches, etc.) in which selected components from one column (primary column) are transferred to a secondary column differing in characteristics (film thickness, polarity, capacity, etc.) from the first column.

3.2.7 *WCOT column*, *n*—wall-coated open tubular, a type of capillary gas chromatographic column prepared by coating the inside of the capillary wall with a specified thin film of stationary phase. The coatings used are either 100 % polydimethyl siloxane or 5 % phenyl-polydimethylsiloxane.

3.2.7.1 *apolar column*, *n*—polydimethylsiloxane nonpolar column used as a pre-column.

3.2.7.2 *PLOT column-oxygen selective*, *n*—porous-layer open tubular which is an oxygenate selective capillary gas-solid chromatographic column. It is used as an analytical column.

4. Summary of Test Method

4.1 An appropriate internal standard of a product that is not present in refinery streams, such as 1,2-dimethoxy ethane (1,2-DME), is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a 4-port switching valve. The sample first passes onto an apolar (non-polar) polydimethylsiloxane WCOT column that performs a pre-separation of the trace oxygenates and elutes unwanted high boiling hydrocarbons to vent. The oxygenates and the DME are transferred to the analytical oxygen selective column by the switching valve. While the oxygenates and the DME are eluting from the analytical column, the inlet's carrier gas is used to elute the hydrocarbons from the pre-column to yield a stable baseline for the next analysis. The auxiliary pressure controller is used to provide carrier gas to the analytical column during the analysis.

4.2 The eluted components [Table 1](#) are detected by one or two flame ionization detectors. In the single detector Configuration A ([Fig. 1](#)), only the components eluting from the analytical column are analyzed. In the two detector Configuration B ([Fig. 2](#)), detector one is used to monitor the apolar elution and aid in setting “heart-cut” times for specific oxygenates while the second detector is used to monitor the analytical column elution and also for the quantitation of the oxygenates. The second detector response is proportional to the oxygenates and DME components concentration. The signal is recorded, the peak areas are measured, and the concentration of each oxygenate is calculated with reference to the internal standard.

4.3 Alternatively, a fluidic switching system, Configuration C ([Figs. 3 and 4](#)) may be used instead of valve switching. In this system, the two columns are joined by a zero dead volume (ZDV) tee purged by an auxiliary carrier source. At injection, the auxiliary flow is low, and the inlet flow is sufficient so that at the midpoint where the two columns join, the flow is the required flow to transfer the oxygenates to the PLOT column. Thus, there is forward flow through the pre-column and the analytical column. Once the oxygenates have passed through to

TABLE 1 Component List with Retention and Calibration Characteristics for WCOT/PLOT Column Set Using Conditions of [Table 2](#)^A

Component	RT (min)	Mol Wt	BP (°C)	Slope	y-Int	Corr. Coef.
ETBE	12.7	102.2	70 to 72	1.919	-0.02	0.999
MTBE	12.8	88.2	55 to 56	1.689	0.01	0.999
DIPE	12.9	102.2	68 to 69	2.124	-0.06	0.999
TAME	13.6	102.2	85 to 86	2.023	-0.02	0.999
Methanol	15.6	32.0	65	0.779	-0.09	0.997
Ethanol	18.7	46.1	78	1.352	0.19	0.999
iso-Propanol	22.2	60.1	81 to 83	1.504	-0.06	0.999
n-Propanol	22.2	60.1	97
t-Butanol	23.8	74.1	82	1.951	-0.12	0.999
s-Butanol	23.8	74.1	98
iso-Butanol	23.8	74.1	117
n-Butanol	24.4	74.1	118	1.906	-0.05	0.999
tert-Pentanol	25.1	88.1	102	2.148	-0.04	0.998
1,2-DME	26.0	90.1	85

^A For coeluting compounds the response is assigned to the first peak listed. Values may be different for different instruments.

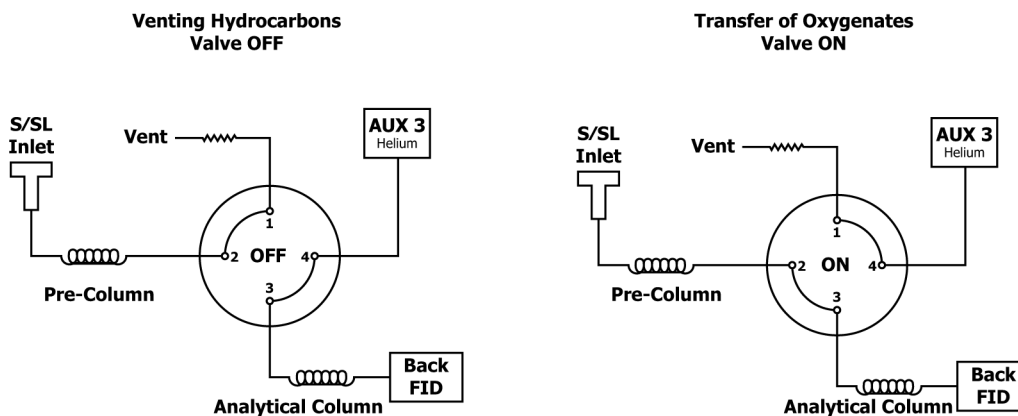


FIG. 1 Schematic of Chromatographic System—Configuration A

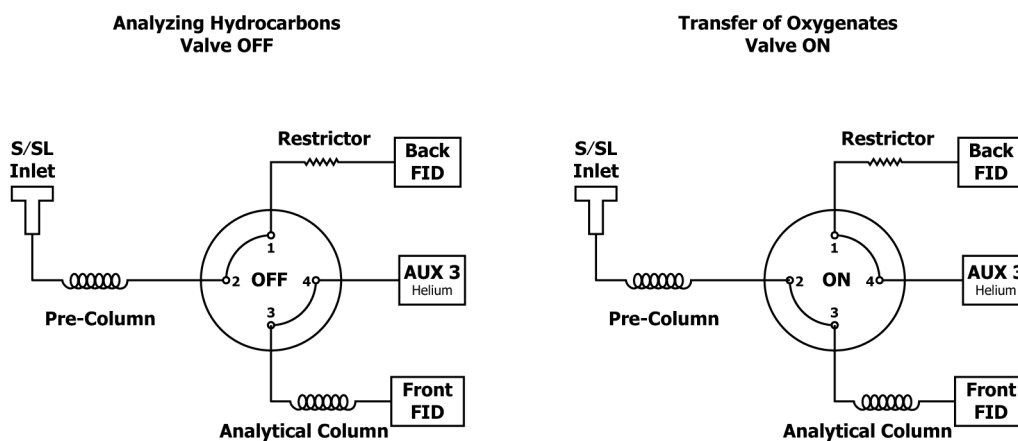


FIG. 2 Schematic of Chromatographic System—Configuration B

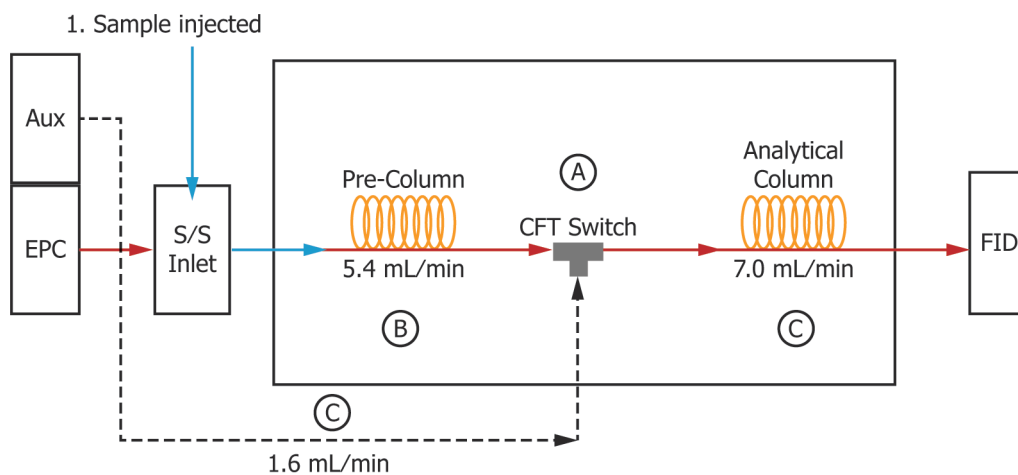


FIG. 3 Fluidic Switch Schematic—Oxygenate Transfer

the analytical column, the inlet flow is decreased and the auxiliary flow is increased, which results in backflushing the pre-column through the split vent of the front inlet while the analytical column continues the separation.

5. Significance and Use

5.1 The analysis of trace oxygenates in automotive spark-ignition engine fuel has become routine in certain areas to

ensure compliance whenever oxygenated fuels are used. In addition, test methods to measure trace levels of oxygenates in automotive spark-ignition fuel are necessary to assess product quality.

6. Apparatus

6.1 *Chromatograph*—A multidimensional gas chromatographic system, which is able to adequately resolve oxygenates