Designation: D4864 – 14

Standard Test Method for Determination of Traces of Methanol in Propylene Concentrates by Gas Chromatography[1]

This standard is issued under the fixed designation D4864; 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 methanol in propylene concentrates in the range of approximately 4 mg/kg to 40 mg/kg (parts-per-million by mass).

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

NOTE 1—There is no direct acceptable SI equivalent for screw threads.

1.3 *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.* Specific warning statements are given in 11.1.1, 11.2.1, and 12.11.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

E260 Practice for Packed Column Gas Chromatography

3. Terminology

3.1 *Definitions:*

3.1.1 *propylene concentrate*—concentrate containing more than 90 % propylene.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *outage tube*—a length of tubing, usually metal, attached to the inside of a valve on a high pressure sampling cylinder such that a fixed percentage of liquid may be expelled from the cylinder to create a specified ullage or vapor space for safety in storage, handling, and transportation.

3.2.1.1 *Discussion*—Typically the outage tube is designed to allow a ullage or vapor space of 15 % to 20 % of the volume of the sample cylinder.

4. Summary of Test Method

4.1 A known mass of water is pressured into a sample cylinder containing a known amount of liquified propylene concentrate. The contents in the cylinder are shaken and the water/methanol phase is withdrawn. A reproducible volume of the extract is then injected into the analytical column of a gas chromatograph (GC) equipped with either a thermal conductivity or a flame ionization detector. The methanol concentration is calculated from the area of the methanol peak using calibration and extraction factors obtained from synthetic blends of known methanol content.

5. Significance and Use

5.1 Methanol is a common impurity in propylene concentrate. It can have a deleterious effect on various processes that use propylene concentrate as a feedstock.

6. Interferences

6.1 There are no known interferences using the GC columns referenced in this test method. However, any water-soluble component that co-elutes with methanol on any other GC column used would interfere.

7. Apparatus

7.1 *Gas Chromatograph*—Any GC equipped with either flame ionization or thermal conductivity detectors with an overall sensitivity sufficient to detect at least 4 mg/kg of methanol.

7.2 *Column*—Any GC column that separates methanol from water, other alcohols, and any co-extracted hydrocarbons.

NOTE 2—See Table 1 for a suitable list of columns and Fig. 1 and Fig. 2 for examples of chromatograms. Also, refer to Practice E260 for typical instructions in preparing such columns. Alternatively, columns can be purchased from commercial sources.

7.3 *Data Handling System*—Any commercially available GC integrator or GC computer system capable of accurately integrating the area of the methanol peak is satisfactory.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.D0.03 on Propylene.

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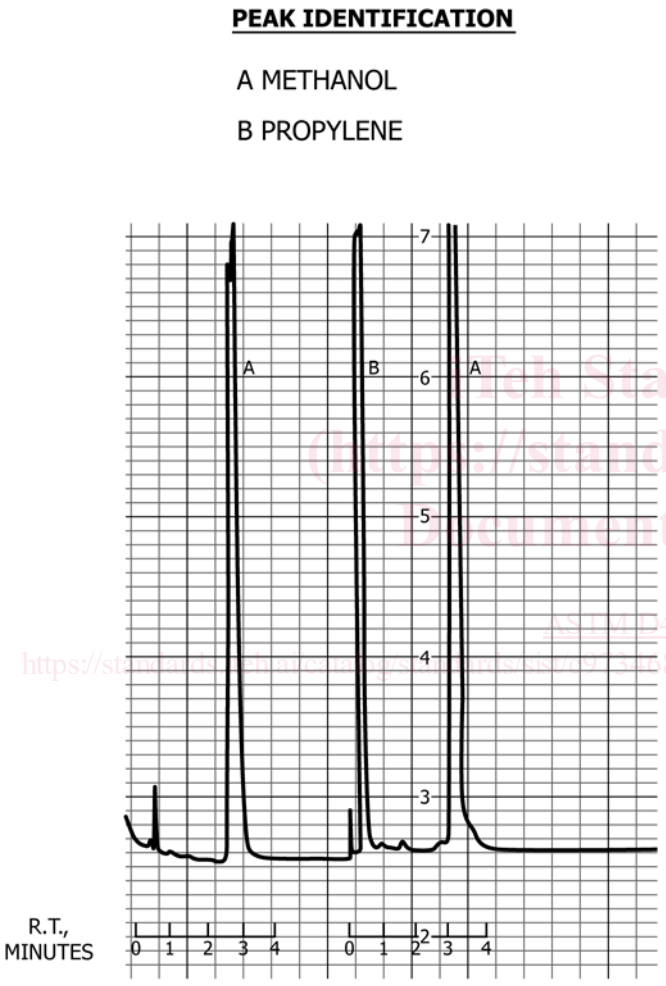
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

TABLE 1 Suitable Gas Chromatographic Columns and Temperatures[A]

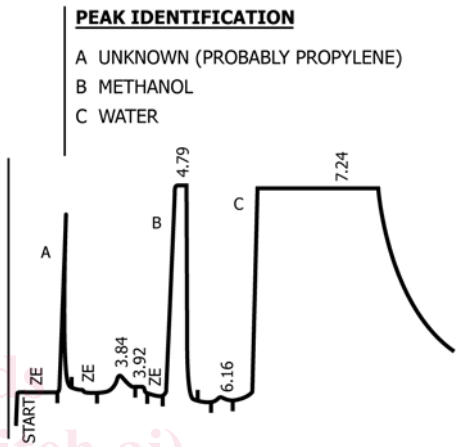
Column Number	Column Size, m × mm	Tubing Type	Packing	Coating, μm Thickness	Oven Temperature,° C
1	1.22 × 6.35 O.D.	SS	15 % Carbowax 1540 on 60/80 Chromosorb W AW	...	90
2	3.05 × 4.76 O.D.	SS	80/100 mesh Porapak QS	...	100
3	3.05 × 6.35 O.D.	Cu	10 % Carbowax 1540 on 30/60 mesh Chromosorb T	...	120
4	6.10 × 6.35 O.D.	Cu	10 % Carbowax 1540 on 30/60 mesh Chromosorb T	...	120
5	1.83 × 2 I.D.	glass	10 % Carbowax 20 M on 80/100 Chromosorb W AW	...	70
6	15 × 0.53 I.D.	fused silica	...	J&W DB-5, 1.5	70 to 120 at 2°/min

[A]These six columns have been tested cooperatively and have been found suitable for use with this test method.



NOTE 1—Column used: No. 5 of Table 1; detector: flame ionization.

FIG. 1 Chromatograms of Water/Methanol Standard and Water/Methanol/Propylene Extract[A]



NOTE 1—Column used: No. 4 of Table 1; detector: thermal conductivity.

FIG. 2 Chromatogram of Water/Methanol/Propylene Extract

7.4 *Recorder*—A strip-chart recorder with a full scale response of 2 s or less and a maximum noise rate of ±0.3 % full scale.

7.5 *Sample Cylinders,* 300 mL capacity, stainless steel, Type DOT 3E (12409 kPa (1800 psig) working pressure).

7.6 *Balances*—Any types capable of weighing a 300 mL sample cylinder and contents accurately to 0.1 g and a 25 mL volumetric flask and contents accurately to 0.0001 g.

7.7 *Plug Valve,* ¼ in. male NPT or optionally, ¼ in. male NPT to 6.35 mm outside diameter (¼ in.) tubing. (See 10.2.1.)

7.8 *Shut-off Valves,* ¼ in. male NPT to 6.35 mm outside diameter (¼ in.) tubing.

7.9 *Regulating Valves,* ¼ in. male NPT and ¼ in. male NPT to ¼ in. female NPT.

7.10 *Hex Nipple,* SS, ¼ in. male NPT by 102 mm (4 in.) long.

7.11 *Hex Coupling,* SS, ¼ in. female NPT by 30 mm (1.2 in.) long.

7.12 *Brass Cap,* ¼ in. NPT or optionally, a tube fitting nut, 6.35 mm outside diameter (¼ in.). (See 10.2.1.)

7.13 *Septum,* TFE-fluorocarbon lined, 11 mm diameter.

7.14 *Syringes,* 10 μL and 25 μL.

8. Reagents and Materials

8.1 *Methanol,* reagent grade or better.

8.2 *Propylene,* 92 % plus purity containing <0.2 mg/kg (ppm mass) methanol.

9. Sampling

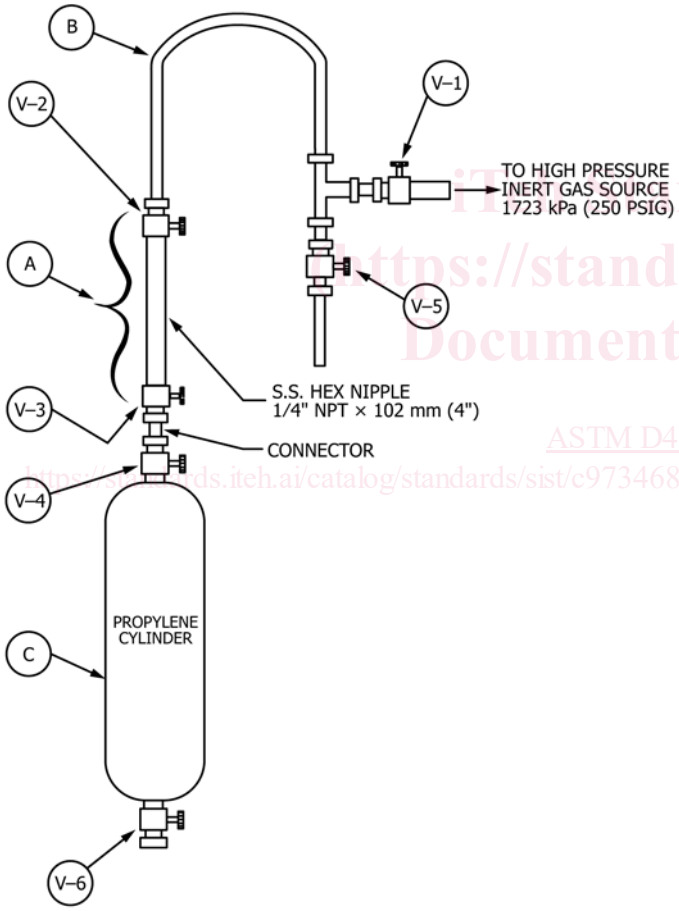
9.1 The propylene concentrate sample shall be in the liquified state and be representative of the material in the

storage tank or process line. Also, for purposes of this method as well as for safety considerations, there must be a vapor space of about 15 % in the sampling container. It is recommended that sampling cylinders of the type listed in Section 7 be used. They can be equipped with an outage tube to effect the 15 % vapor space requirement.

10. Preparation of Apparatus

10.1 Prepare a water injection device. A suitable device is shown in Fig. 3. However, any other device that will deliver from 8 g to 15 g of water may be used.

10.2 Prepare a 300 mL sample cylinder for use as a methanol cylinder, as shown in Fig. 4. (This cylinder must not contain an outage tube.) Drill a 3 mm to 4 mm (approximately ⅛ in.) hole in a ¼ in. NPT brass cap, insert an 11 mm septum into it, and screw it onto the plug valve.



(A) Water injection device
(B) 6.35 mm OD (¼ in.) SS tubing
(C) Sample cylinder containing propylene
(V–1) & (V–5) Shut off valves, ¼ in. male NPT to 6.35 mm OD (¼ in.) tubing
(V–2) & (V–3) Regulating valves, ¼ in. male NPT to ¼ in. female NPT
(V–4) & (V–6) Regulating valves, ¼ in. male NPT to ¼ in. male NPT

FIG. 3 Water Injection Assembly

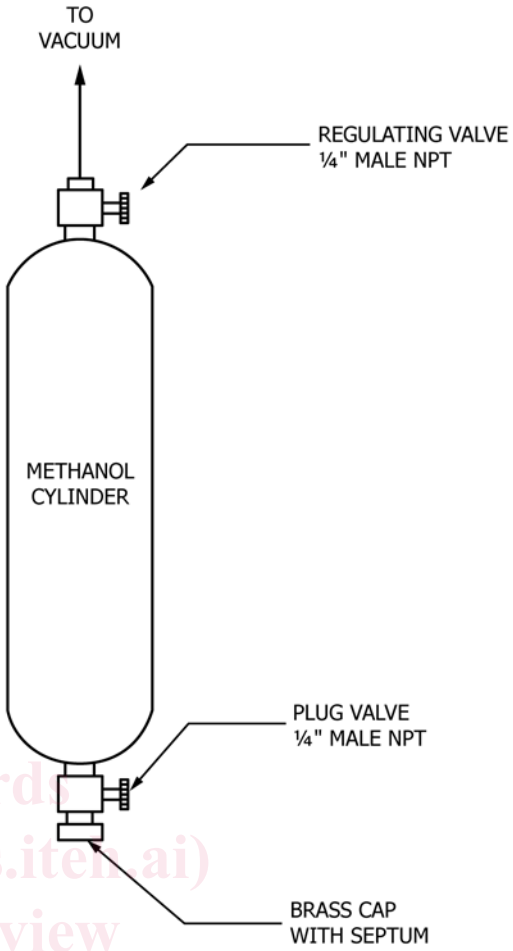


FIG. 4 Methanol Cylinder Extraction Factor Determination

10.2.1 As an alternative, the cylinder may be equipped with ¼ in. male NPT to a 6.35 mm (¼ in.) outside diameter tubing plug valve. Then a 6.35 mm tube fitting nut can be used with the septum, thus avoiding the necessity of drilling a brass cap.

10.3 Set up the chromatograph in accordance with the manufacturer's recommendations. Install the analytical column and adjust the gas flows and temperatures so that methanol will elute at the desired time. Condition the column at operating conditions until a stable baseline is recorded at the required sensitivity.

11. Calibration

11.1 *Determination of Methanol Response Factor*—Prepare several aqueous solutions of methanol in the same concentration range as expected for samples to be analyzed.

NOTE 3—This should be approximately 40 mg/kg to 400 mg/kg (ppm mass) on the basis of propylene concentrate sample sizes of 100 g to 120 g, water extract volumes of about 10 g, and methanol concentrations in the propylene concentrate of 4 mg/kg to 40 mg/kg.

11.1.1 *Methanol Stock Solution*—Weigh an empty volumetric flask of at least 25 mL capacity to the nearest 0.0001 g. Add 20 mL of deionized water to the flask and reweigh. Finally, add 2 mL of methanol and again reweigh. Stopper and mix thoroughly. This should contain approximately 73 000 mg/kg