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 The contents in the cylinder are shaken and the water/methanol phase is withdrawn.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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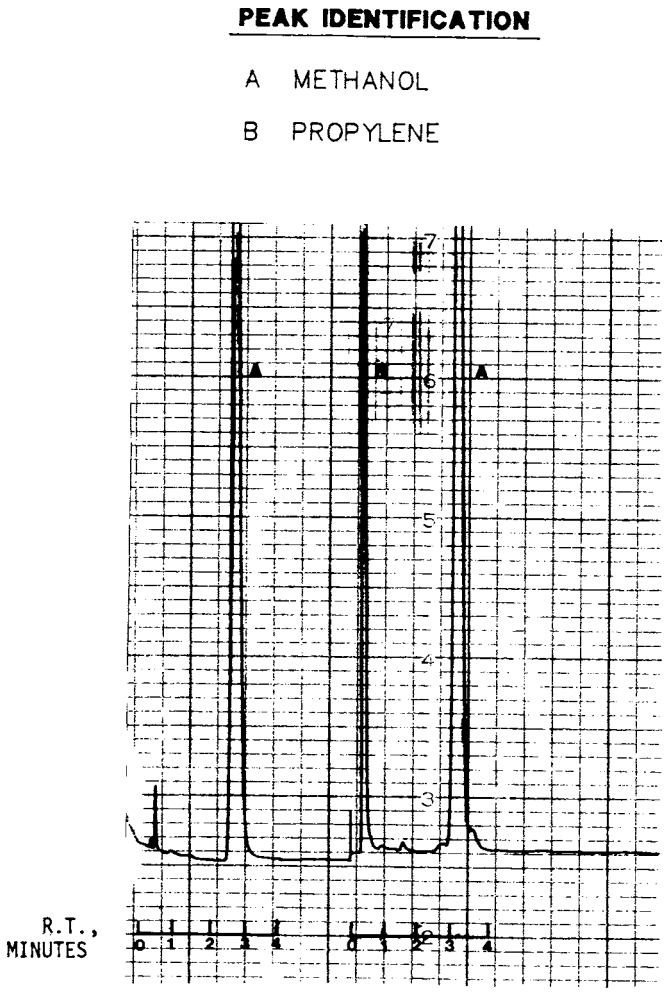
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

TABLE 1 Suitable Gas Chromatographic Columns and Temperatures[A]

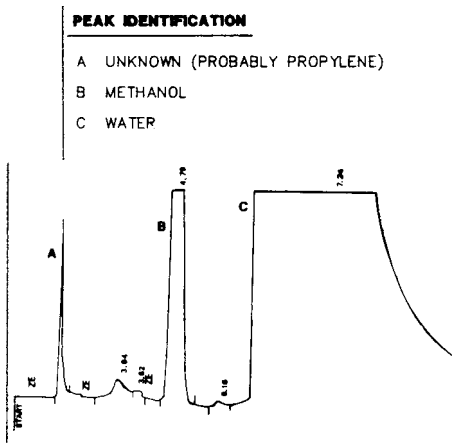
Column Number	Column Size, m × mm	Tubing Type	Packing	Coating, μm Thickness	Oven Temperature,° C
1	1.22 × 6.35 O.D.	SS	15 % Carbowax 1540 on 60/80 Chromosorb W AW	...	90
2	3.05 × 4.76 O.D.	SS	80/100 mesh Porapak QS	...	100
3	3.05 × 6.35 O.D.	Cu	10 % Carbowax 1540 on 30/60 mesh Chromosorb T	...	120
4	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

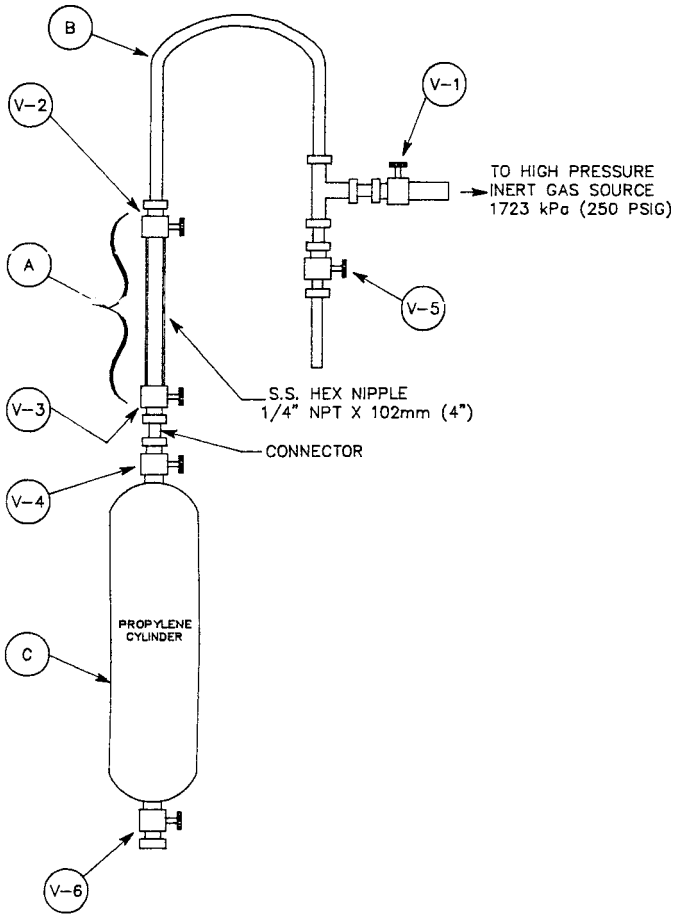
as well as for safety considerations, there must be a vapor space of about 15 % in the sampling container. It is recommended that sampling cylinders of the type listed in Section 7 be used. They can be equipped with an outage tube to effect the 15 % vapor space requirement.

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.

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.



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

FIG. 3 Water Injection Assembly

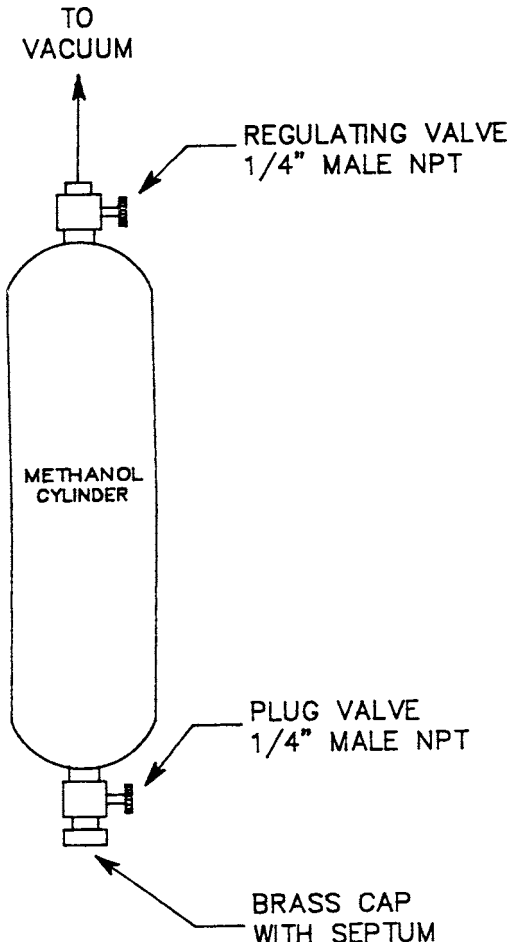


FIG. 4 Methanol Cylinder Extraction Factor Determination

10.3 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 (ppm by mass) of methanol. Calculate the exact concentration

from the actual mass used. (**Warning—**Methanol is toxic and flammable. Use with adequate ventilation and keep away from ignition sources.)

NOTE 4—Refer to Practice D4307 for additional information in preparing this solution and the calibration solution in 11.1.2.

11.1.2 *Methanol Calibration Solutions*—In similar manner, make serial dilutions by mass until two different concentrations in the range from 40 mg/kg to 400 mg/kg are prepared.

11.1.3 With the GC at the proper operating conditions, inject an appropriate quantity of each calibration solution, in duplicate, and obtain the area of the methanol peak.

NOTE 5—The quantity of solution to be injected will depend largely on the type of detector in use. It varies from about 3 µL for FIDs to 25 µL for TCDs.

11.1.4 For each solution, calculate the response factor for methanol as follows:

$$F = C/H \quad (1)$$

where:

F = methanol response factor,
C = concentration of methanol, mg/kg, in the blend, and
H = area of the methanol peak (average of duplicate injections).

11.1.5 When the response factors at the two concentrations agree within 5 %, average them for use in the final calculation given in Section 13.

11.2 *Determination of Methanol Extraction Factor*—Since the methanol is not extracted quantitatively due to solubility competition between the water and the propylene, the extraction efficiency must be determined experimentally as follows.

11.2.1 Collect 100 g to 120 g (190 mL to 230 mL) of methanol-free propylene in a tared 300 mL sample cylinder. Reweigh the cylinder to ensure that it contains the proper amount. (**Warning—**Liquified propylene concentrate is at high pressure, can cause frostbite, and is flammable. Use appropriate care in handling.)

11.2.2 As shown in Fig. 4, attach the opposite end of the septum-equipped methanol cylinder to a vacuum source. Be sure that this assembly is leak-free.

11.2.3 Open both valves and evacuate the cylinder up to the septum. Then close the plug valve (next to the septum) and continue the evacuation. Finally, close the other cylinder valve, disconnect the cylinder from the vacuum source, and weigh it to the nearest 0.1 g.

11.2.4 Flush a 10 µL or 25 µL syringe several times with methanol, then fill it to the desired volume (see Table 2), wipe off the tip, pull the plunger back about 1 µL, and weigh it to the nearest 0.0001 g.

TABLE 2 Methanol Injection Sizes

Methanol Volume, µL	Mass, mg	Equivalent Concentration, mg/kg for 100 g propylene
5	4	36
10	8	72
15	12	108
20	16	144

11.2.5 Open the cylinder plug valve at the septum and immediately inject the methanol in the syringe through the septum into the cylinder. Close the valve and immediately reweigh the syringe to determine the amount of methanol injected. The difference between this mass and that obtained in 11.2.4 is the mass of methanol injected, W_1.

11.2.6 Cool the evacuated cylinder to about 20 °C below the temperature of the propylene concentrate cylinder.

11.2.7 As shown in Fig. 5, connect the cylinder containing propylene to the evacuated cylinder containing methanol via a hex coupling, a short length of 6.35 mm (¼ in.) outside diameter SS tubing, or any other suitable fitting. Before

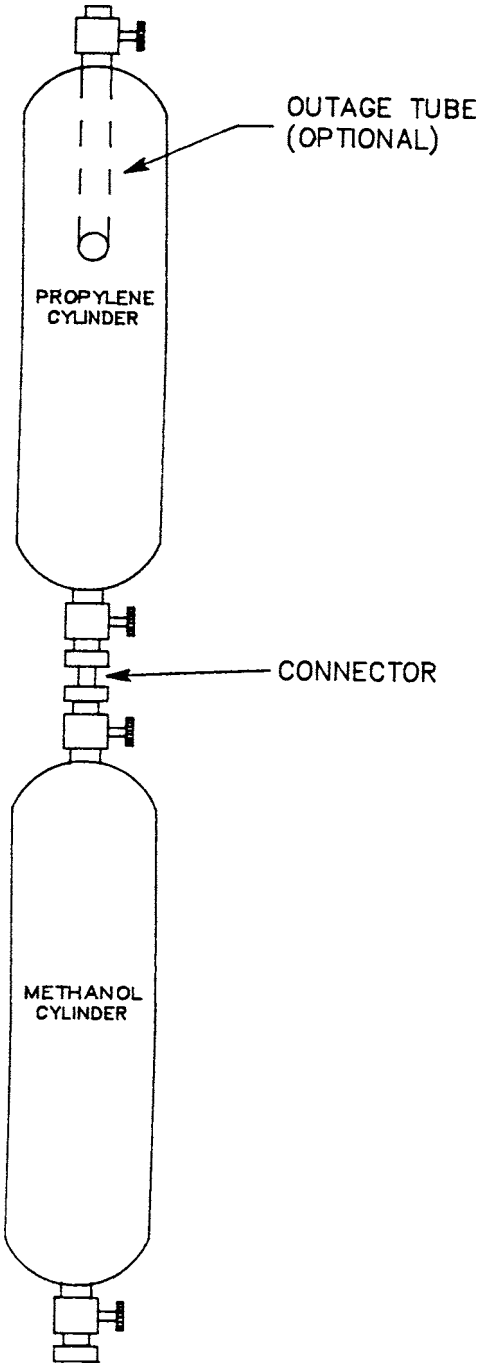


FIG. 5 Cylinders Assembly Extraction Factor Determination

tightening, flush the connector with a small amount of propylene concentrate by briefly opening the lower valve on the propylene concentrate cylinder.

11.2.8 With both cylinders in a vertical position and the propylene concentrate cylinder on top, open the valves between them (*propylene concentrate cylinder first*) and allow the liquified propylene concentrate to flow into the evacuated cylinder.

11.2.9 Close the valves, disconnect the cylinders, and allow the lower cylinder to warm to room temperature. Wipe off any water condensation and allow to dry.

11.2.10 Weigh the cylinder containing the methanol and propylene concentrate blend to the nearest 0.1 g. The difference between this mass and that obtained in 11.2.3 is the mass of methanol and propylene concentrate, W_2. Calculate the concentration of methanol as follows:

$$C = (W_1 \times 10^6)/W_2 \quad (2)$$

where:

C = concentration of methanol, mg/kg,
W_1 = mass of methanol injected, g, and
W_2 = mass of propylene concentrate plus methanol, g.

11.2.11 Shake the cylinder vigorously to mix the propylene concentrate and methanol. Then extract the methanol and analyze the extract as described in 12.2 – 12.13. Analyze the extract in duplicate and average the methanol peak areas.

11.2.12 Calculate the methanol content of the extract as described in 13.1, but exclude F_x, the methanol extraction factor.

11.2.13 Calculate the methanol extraction factor as follows:

$$F_x = C/D \quad (3)$$

where:

F_x = methanol extraction factor,
C = methanol concentration calculated in Eq 2, and
D = methanol concentration calculated in 11.2.10.

NOTE 6—It is recommended that the extraction procedure be repeated at a different concentration to verify the accuracy of the factor. Extraction factors of 1 to 2 are typical.

12. Procedure

12.1 Weigh the sampling cylinder containing at least 100 g of propylene concentrate to the nearest 0.1 g.

NOTE 7—When practical, it is advisable to weigh the sampling cylinder before sampling to obtain a tare mass.

12.2 Pressure deionized water into the injection device in a vertical position from the bottom and close the valves.

12.3 As shown in Fig. 3, connect the injection device to the sample cylinder using a hex coupling or other suitable device.

12.4 Attach the other end to an inert gas source at 1724 kPa (250 psig) and purge the lines between V_2 and V_5.

12.5 Close V_5 and tighten the connection at V_2.

12.6 Pressure the water into the cylinder by opening Valves V_1, V_2, V_3, and V_4, in that order.

12.7 Close valves V_1 and V_4 and depressure the device via V_5. Then disconnect the cylinder.

12.8 Remove any residual water from the outlet of V_4 and reweigh the cylinder to 0.1 g. The difference between this mass and that in 12.1 is the mass of the water, W.

12.9 Shake the cylinder vigorously for at least 10 min.

12.10 Clamp the cylinder in a vertical position and allow the aqueous phase to settle. (When the cylinder contains an outage tube, it must be at the top of the cylinder.)

12.11 Carefully open the bottom valve and drain the aqueous phase containing the methanol into an appropriate container (vial or flask) and cap it. (**Warning—**As soon as the aqueous phase drains, high-pressure liquified propylene concentrate will surge out.)

12.12 With the GC at the proper operating conditions, inject the appropriate size of the aqueous extract for the GC and calibration being used.

12.13 Safely vent off the remaining propylene in the sample cylinder and reweigh it to 0.1 g (unless the cylinder was already tared.) The difference between this mass and that in 12.1 is the mass of the propylene concentrate extracted, G.

13. Calculation

13.1 Calculate the methanol content of the propylene concentrate using the following equation:

$$\text{Methanol, mg/kg (ppm mass)} = (A \cdot F \cdot F_x \cdot W)/G \quad (4)$$

where:

A = area of methanol peak,
F = methanol response factor for the sample size used (Eq 1),
F_x = methanol extraction factor (Eq 3),
W = mass of water used in the extraction, g, and
G = mass of propylene concentrate extracted, g.

14. Precision and Bias[3]

14.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

14.1.1 *Repeatability*—The difference between successive results by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following value only in 1 case in 20:

Repeatability = The maximum allowable ratio of the larger to the smaller result is 2.4.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in 1 case in 20:

Reproducibility = The maximum allowable ratio of the larger to the smaller is 8.0.

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007 and Research Report RR:D02-1243.

14.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for this procedure for measuring methanol, the bias is not available for this test method.

15. Keywords

15.1 gas chromatography; methanol; propylene

SUMMARY OF CHANGES

Subcommittee D02.D0 has identified the location of selected changes to this standard since the last issue (D4864 – 90 (2013)) that may impact the use of this standard. (Approved July 15, 2014.)

(1) Revised definition of "outage tube."

(2) Changed "weight" to "mass" throughout.