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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Analysis of Methanol[1]

This standard is issued under the fixed designation E 346; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover chemical and physical tests for measuring the quality of methanol and appear in the following order:

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Acidity	7 to 9
Carbonizables	10 to 18
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Ethanol	37 to 47
Acetone	48 to 55
Trimethylamine	56 to 65

1.2 *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 hazards statements are given in Sections 5 and 15 and in Note 3, Note 4, and Note 19.

2. Referenced Documents

2.1 *ASTM Standards:*

D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals[2]

D 1078 Test Method for Distillation Range of Volatile Organic Liquids[3]

D 1193 Specification for Reagent Water[4]

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)[3]

D 1363 Test Method for Permanganate Time of Acetone and Methanol[3]

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[3]

D 1722 Test Method for Water Miscibility of Water-Soluble Solvents[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 203 Test Method for Water Using Karl Fischer Reagent[2]

E 300 Practice for Sampling Industrial Chemicals[2]

E 1140 Practice for Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use in Gas Chromatography[2]

3. Significance and Use

3.1 These test methods are suitable for manufacturing control and for determining compliance with specification limits for the properties designated by the test methods. For those test methods that use the procedure given in other ASTM methods, those test methods should be consulted for additional information on the significance, use, and possible interferences.

4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean Type II or III reagent water conforming to Specification D 1193. It is essential that the reagent water be free of ammonia when used in the method for acetone.

5. Hazards

5.1 Methanol is toxic both as a liquid and as a vapor, and is dangerous if not properly handled. Avoid any skin contact.

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[1] These test methods are under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and are the direct responsibility of Subcommittee E15.53 on Alcohols and Polyalcohols.

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

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

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

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Clothing contaminated with methanol should be removed immediately. Any body exposure to methanol requires immediate medical attention.

5.2 Methanol is flammable and its vapor is explosive in the range from 6.0 to 36.5 volume % in air. Any spills should be flushed away promptly with water.

6. Sampling

6.1 Sampling is not within the scope of these test methods. It should be understood, however, that reference to a "sample" means a representative portion of methanol contained in a single container submitted for test. The sample submitted should be sufficient to make all tests without reuse of any fraction. For details of sampling methanol, refer to Practice E 300.

ACIDITY

7. Procedure

7.1 Determine the acidity of the methanol as acetic acid using the titration method as described in Test Method D 1613.

8. Report

8.1 For concentrations of acetic acid at the 0.0010 % level, report the results to the nearest 0.0001 weight %. For concentrations at the 0.010 % level, report the results to the nearest 0.001 weight %.

9. Precision and Bias

9.1 *Precision*—The following criteria should be used for judging the acceptability of results (Note 1):

9.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the absolute percentage value in Table 1 at the indicated degrees of freedom (df). The 95 % limit for the difference between two such runs is the absolute percentage value in the table.

9.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the absolute percentage value in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the absolute percentage value in the table.

9.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the absolute percentage value in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the absolute percentage value in the table.

NOTE 1—The above precision estimates are based on an interlaboratory study performed on two samples of methanol containing approximately 0.0010 and 0.01 % acetic acid. A total of nine laboratories cooperated in the studies in which duplicate determinations were performed on each of two days. Practice E 180 was used in developing these precision estimates.

9.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

CARBONIZABLES

10. Scope

10.1 This test method describes a procedure for detecting the presence of impurities in methanol that carbonize or darken in the presence of concentrated sulfuric acid. The test method is applicable to methanol having a carbonizables content in the range from 0 to 70 on the platinum-cobalt scale (see Test Method D 1209).

11. Summary of Test Method

11.1 Methanol is mixed with a known volume of concentrated sulfuric acid under controlled conditions. The color formed by the action of the acid on the carbonizable impurities in the methanol is estimated by comparison of the test mixture with platinum-cobalt color standards.

12. Significance and Use

12.1 Because this test is designed to measure low concentrations of impurities that carbonize or darken in the presence of concentrated sulfuric acid, erroneously high results may be obtained if all glassware is not cleaned as described in the procedure.

13. Apparatus

13.1 *Erlenmeyer Flask*, 125-mL borosilicate glass.

13.2 *Nessler Tubes*, 50-mL high form, matched.

13.3 *Ring Stand*.

13.4 *Buret*, 25-mL, with TFE-fluorocarbon stopcock.

NOTE 2—A 25-mL automatic buret graduated in 0.1-mL increments provides a safe convenient way of dispensing the sulfuric acid and protects the acid from dust and other contamination.

13.5 *Electric Stirrer and Bar*.

14. Reagents

14.1 *Sulfuric Acid*—Concentrated sulfuric acid (sp gr 1.84).

14.2 *Platinum-Cobalt Stock Solution and Color Standards*, made in accordance with Test Method D 1209.

15. Hazards

15.1 Concentrated sulfuric acid is corrosive; contact with the body is to be avoided at all times. Use proper protective equipment, including adequate eye protection. If the eyes are affected or if a burn results, obtain immediate medical attention.

TABLE 1 Acidity Precision Values, % Acetic Acid

Level,%	Repeatability			Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
0.0010	0.000067	18	0.0002	0.000065	18	0.0002	0.00024	8	0.00007
0.010	0.00034	18	0.001	0.000437	18	0.001	0.00061	8	0.002

16. Procedure

16.1 All glass apparatus used for this test must be kept free of materials which produce color with sulfuric acid. Clean all glassware in a dichromate-sulfuric acid cleaning solution followed by rinsings with tap water and reagent water. Dry with clean air or rinse with methanol that is known to give little or no color with sulfuric acid.

NOTE 3—**Caution:** Do not use acetone to dry apparatus.

16.2 Transfer 50 mL of the proper platinum-cobalt color standard into one of the matched 50-mL Nessler tubes.

16.3 Pipet 30 mL of the sample into a 125-mL Erlenmeyer flask.

16.4 Add, at a uniform rate, 25 mL of H_2SO_4 to the sample while stirring constantly using an electric stirrer and stirring bar. The total time of the acid addition shall be 5 min ± 30 s.

NOTE 4—**Caution:** Do not cool the mixture.

16.5 Allow the mixture to stand for 15 min ± 30 s at room temperature, pour the mixture from the flask into a 50-mL Nessler tube and compare the color of the sample to the proper platinum-cobalt standard by looking down through the longitudinal axis of the tubes upon a white or mirrored surface at such an angle that light is reflected through the column of liquid. Hold the tubes at some convenient height 50 to 150 mm (2 to 6 in.) from the surface.

17. Report

17.1 According to the type of specification used, this test can be made to give specific color readings or be simply a go, no-go test.

17.2 When specific color readings are required, report the platinum-cobalt color to the nearest 5 units. Averages of duplicate determinations should be reported to the nearest 2.5 units.

18. Precision and Bias

18.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 5):

18.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 1.7 units at 21 df. The 95 % limit for the difference between two such runs is 5 units.

18.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

18.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value shown in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 5—The precision estimates in Table 2 are based on an interlaboratory study performed on three samples at the color levels listed. One analyst in each of seven laboratories performed duplicate measurements on each of two days. Practice E 180 was used in developing these precision estimates.

18.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

COLOR

19. Procedure

19.1 Determine the color of the methanol as described in Test Method D 1209.

20. Report

20.1 Estimate and report the color of the methanol to the nearest 1 Pt-Co unit.

21. Precision and Bias

21.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 6):

21.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.7 units at 36 df. The 95 % limit for the difference between two such runs is 2 units.

21.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

21.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value shown in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 6—The above precision estimates are based on an interlaboratory study performed on two samples of methanol having Pt-Co color values of 0 and 10 respectively. One analyst in each of eight laboratories performed duplicate measurements on each of two days. Practice E 180 was used in developing these precision estimates.

21.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

TABLE 2 Carbonizables Precision Values, Pt-Co Units

Pt-Co Level	Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
5	1	13	3	2	6	5
15	1	13	3	3	6	10
60	1	13	3	5	6	15

TABLE 3 Color Precision Values, Pt-Co Units

Pt-Co Level	Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
0 to 2	<1	10	2	1.7	9	5
3 to 10	<1	8	2	2.0	7	6

DISTILLATION RANGE

22. Procedure

22.1 Determine the distillation range of the methanol as described in Test Method D 1078. ASTM Solvents Distillation Thermometer 39°C (range 48 to 102°C with 0.2 subdivisions) should be used.

22.2 Use a *K* value of 0.033 for calculating the barometric correction to be applied to each corrected thermometer reading for the following volumes of distillate: 1st drop, 5, 50, 95 mL and dry point. The dry point is defined as the temperature at the instant the last drop of methanol evaporates from the lowest point in the distillation flask disregarding any liquid clinging to the side of the flask. If the boiling range does not exceed 2°C, a simpler correction is permissible, such as by filling the condenser bath with water of the appropriate temperature shown in the Temperatures table of Test Method D 1078.

23. Report

23.1 Report the corrected temperatures to the nearest 0.1°C at each volume listed under 22.2 or at such other volumes as required by specifications for the methanol being tested.

24. Precision and Bias

24.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 7):

24.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

24.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

24.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 7—The above precision estimates are based on an interlaboratory study performed on two samples containing approximately 80, 90, and 95 % sulfuric acid. One analyst in each of nine laboratories performed duplicate determinations on each of two days. Practice E 180 was used in developing these precision estimates.

24.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

PERMANGANATE TIME

25. Procedure

25.1 Determine the permanganate time of the sample as described in Test Method D 1363.

26. Report

26.1 If the residual pink color of the sample is greater than the standard, report the permanganate time as "greater than *X* min." If the residual pink color of the sample is equal to that of the standard, report the permanganate time as "*X* min." If the residual pink color of the sample is less than the standard, report as "less than *X* min." In each case "*X* min" is the minimum time specified for the material being tested.

NOTE 8—An estimate of the total permanganate time may be made by continuing to observe the sample beyond the minimum specification limit until the color of the sample matches that of the standard. Report the permanganate time to the nearest whole minute.

27. Precision and Bias

27.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 9):

27.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 1.4 min at 60 df. The 95 % limit for the difference between two such runs is 4 min.

27.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 5 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

27.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by

TABLE 4 Distillation Range Precision Values, °C

	Repeatability			Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
First drop	0.035	36	0.1	0.049	18	0.1	0.186	8	0.5
5 mL	0.035	36	0.1	0.032	18	0.1	0.118	8	0.3
50 mL	0.035	36	0.1	0.044	18	0.1	0.102	8	0.3
95 mL	0.069	36	0.2	0.093	18	0.3	0.157	8	0.4
Dry Point	0.10	36	0.3	0.066	18	0.2	0.237	8	0.7

TABLE 5 Permanganate Time Precision Values, min

Level, min	Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
40	1	9	3	3	9	8
73	2	9	6	8	9	22
96	4	9	11	11	9	31

analysts in different laboratories, has been estimated to be the value shown in Table 5 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 9—The above precision estimates are based on an interlaboratory study (Note 10) on three samples of methanol having average permanganate times of 40, 73, and 96 min. Two analysts in each of five laboratories performed duplicate runs on each of two days. Practice E 180 was used in developing these precision estimates.

NOTE 10—The precision estimates for permanganate time were provided by an interlaboratory study conducted by ASTM Committee E-1 on Paint and Related Coatings and Materials in 1967.

27.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

SPECIFIC GRAVITY

28. Procedure

28.1 Determine the specific gravity of the methanol sample at 20/20°C as described by the pycnometer procedure in Test Methods D 891.

29. Report

29.1 Report the specific gravity at 20/20°C to the nearest 0.00001 unit.

30. Precision and Bias

30.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 11):

30.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.000028 units at 36 df. The 95 % limit for the difference between two such runs is 0.00008 unit.

30.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000026 units at 18 df. The 95 % limit for the difference between two such averages is 0.00007 units.

30.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00017 units at 8 df. The 95 % limit for the difference between two such averages is 0.00048 units.

NOTE 11—The above precision estimates are based on an interlaboratory study performed on two samples of methanol having a specific gravity at 20/20°C of approximately 0.79267. One analyst in each of nine laboratories performed duplicate determinations on each of two days. Practice E 180 was used in developing these precision estimates.

30.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

WATER

31. Procedure

31.1 Determine water in the methanol sample as described in Test Method E 203.

31.2 Because of the hygroscopic nature of methanol, all care should be taken to protect the sample from atmospheric moisture during transfer from the sample container to the titration vessel.

32. Report

32.1 Report the percentage of water to the nearest 0.001 weight %.

33. Precision and Bias

33.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 12):

33.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0035 % absolute at 40 df. The 95 % limit for the difference between two such runs is 0.010 % absolute.

33.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0053 % absolute at 20 df. The 95 % limit for the difference between two such averages is 0.015 % absolute.

33.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0159 % absolute at 9 df. The 95 % limit for the difference between two such averages is 0.045 % absolute.

NOTE 12—The above precision estimates are based on an interlaboratory study performed on samples containing between 0.030 and 0.100 % water. One analyst in each of ten laboratories performed duplicate determinations on each of two days. Practice E 180 was used in developing these precision estimates.

33.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

WATER MISCIBILITY

34. Procedure

34.1 Determine the water miscibility of the methanol sample as described in Test Method D 1722.

35. Report

35.1 Report sample “passes test” if the methanol-water mixture is as free from cloudiness or turbidity as the blank. If any cloudiness or turbidity is detected after 30 min, report samples as“ fails test.”

36. Precision and Bias

36.1 Since no specific level of impurity is detected by this test, no values are determined from which precision and bias estimates can be made.

ETHANOL

37. Scope

37.1 This test method is applicable to methanol in which the ethanol content is between 0 and 1000 ppm.

38. Summary of Test Method

38.1 The sample is injected into and carried through a single, packed, gas-liquid partition column with a carrier gas (helium). The separated components in the effluent are measured by a flame ionization detector and recorded on a chromatogram. The test method is made quantitative by calculating the ratio of the ethanol peak area to the isopropanol (internal standard) peak area and applying a previously determined ethanol calibration factor.

39. Significance and Use

39.1 No interfering substances have been detected in refined methanol. If present, *n*-propanol or *n*-butanol could interfere with the resolution of the ethanol.

40. Apparatus

40.1 *Gas Chromatograph*, with the following characteristics:

40.1.1 Sample injection port operable at 275°C.

40.1.2 Column oven capable of isothermal operation at 100°C.

40.1.3 Flame ionization detector capable of operating at 275°C.

40.2 *Recorder*, 0 to 1-mV range, 1-s pen speed, chart speed 30 in./h.

40.3 *Column Tubing*, stainless steel, 6 mm (0.25 in.) in outside diameter, 5 mm (0.21 in.) in inside diameter, 0.051-mm (0.020-in.) wall.

40.4 *Column*, 610 cm (20 ft) of the stainless steel tubing, filled with 33 weight % *D*-sorbitol on 80 to 100 mesh, acid-washed orange calcinated diatomite.[6]

40.5 *Syringes*. [7]

40.6 *Serum Bottle*, serum-stoppered, 125-mL.

41. Reagents

41.1 *Compressed Gases*—Air (water-pumped); helium (Grade A); hydrogen (purified).

41.2 *Ethanol*, absolute, USP XVII.

41.3 *Methanol, Ethanol-free*, defined as containing less than 10 ppm ethanol. Prepare the amount wanted by distillation on a 30-plate Oldershaw (or equivalent) column operated on total reflux for several hours. Draw off purified methanol with the column operating at 30:1 reflux ratio.

NOTE 13—To check the ethanol content of the distillate, analyze under the conditions outlined in Section 43, a 10-µL sample of distillate and an 8-µL sample of an aqueous ethanol solution made up to contain 10 ppm ethanol. Compare the ethanol peak of the distillate with that of the solution containing 10 ppm ethanol.

41.4 *Isopropanol*.

41.5 *Internal Standard Solution*—Add 0.5 mL (micro pipet) of isopropanol to about 50 mL of methanol (ethanol-free) in a 100-mL glass-stoppered volumetric flask, fill to volume with the methanol, stopper, and mix thoroughly. Store the isopropanol-methanol internal standard in a 125-mL serum bottle and close with a serum stopper.

41.6 *D-Sorbitol*, purified (maximum operating temperature 150°C).

41.7 *"Chromosorb" P*, [6] acid-washed, 80 to 100 mesh.

42. Preparation of Chromatographic Column

42.1 Dissolve 33 g of *D*-sorbitol in 300 mL of methanol (does not have to be ethanol-free) in a 600-mL beaker on a steam bath. Add, with stirring, 67 g of the acid-washed orange calcinated diatomite to the *D*-sorbitol-methanol solution.

42.2 Continue heating on the steam bath to remove the methanol. Stir frequently. When the residue is sufficiently dry to be free-flowing, transfer it to a shallow drying dish for 4 h in a vacuum oven (or rotating evaporator) at 50 to 60°C. As an alternative the material may be air-dried at room temperature by spreading it out and leaving overnight (16 h).

42.3 Plug one end of the 610-cm (20-ft) length of the stainless steel tubing with glass wool. Add, in any convenient manner, the dried column packing (about 50 g) until the tube is filled with 12.7 mm (½ in.) of the top. Vibrate the tube (manually or mechanically) during filling to assure a minimum of voids. Plug the top of the column with glass wool and install it in the chromatography.

42.4 Condition the column (Note 14) as outlined in Section 43.

NOTE 14—A freshly packed column should come to a stable baseline in 30 to 45 min. A column in routine use should only require 10 min to stabilize.

43. Calibration

43.1 Tare (±0.0001 g) a clean, dry, 100-mL, glass-stoppered volumetric flask. Add 50 mL of ethanol-free methanol and reweigh. Add 0.5 mL (Mohr pipet) of absolute ethanol whose water content is known. Stopper and reweigh; the difference between the last two weighings is the weight of ethanol *E*.

43.2 Bring the flask to volume with ethanol-free methanol, stopper, and reweigh.

43.3 Calculate the percent ethanol (about 0.5 %) in this standard ethanol solution as follows:

$$\text{Ethanol, \%} = \frac{[E \times (100 - A)]}{W} \quad (1)$$

where:

E = weight of ethanol,

[6] "Chromosorb" P, a trademark of the Johns-Manville Products Corp., Celite Div., 22E 40 St., New York, NY, has been found satisfactory for this purpose. It is available from supply houses.

[7] Hamilton Microliter No. 705-N (0.05-mL capacity) and No. 710-N (0.10-mL capacity) have been found satisfactory for this purpose.

A = percent of water in ethanol, and
W = net weight of flask contents.

43.4 Using a syringe, add 10-µL portions of the internal standard solution (see 41.5) to each of six clean, dry, 25-mL, glass-stoppered, volumetric flasks containing about 20 mL of ethanol-free methanol. To the six flasks in series, add (micro pipet or syringe) the following volumes of standard ethanol solution: 0.00, 0.05, 0.10, 0.20, 0.50, and 1.0 mL. Bring the flasks to volume with ethanol-free methanol, stopper each, and mix thoroughly.

43.5 The flask containing 0.00 mL of standard ethanol solution will serve as a blank on the ethanol-free methanol. It is essential, therefore, that the same methanol be used for all dilutions in preparing these standards. The prepared standards cover an ethanol range only to about 200 ppm. If necessary, higher standards can be prepared in the same manner by using larger amounts of the standard ethanol solution.

43.6 Calculate to the nearest 0.1 ppm the ethanol in each standard from the following:

$$\text{Ethanol, ppm} = \frac{B \times C \times 10^4}{24.9} \quad (2)$$

where:
B = ethanol standard, mL
C = percent of ethanol in the standard, and
24.9 = true volume of each standard (25.0 mL flask volume minus 100 µL internal standard).

43.7 Calculate the calibration factor, m, as follows:

43.7.1 Obtain a chromatogram of each of the six ethanol standards by following steps 44.1 through 44.3.

43.7.2 Calculate for each standard the ratio, r, of the area of the ethanol peak to the area of the internal standard solution peak by following steps 45.1 through 45.4.

43.7.3 Correct the ratio, r, for each standard by subtracting the r of the 0.0 ethanol standard (blank). Plot these corrected r values for the standards against their ethanol contents in ppm to determine that the calibration curve passes through the zero point.

43.7.4 Calculate m values as follows:

$$m = r \text{ corrected/ppm ethanol added to standard} \quad (3)$$

Average the m values. (They should agree within 10 % relative.) This average m value is the calibration factor and should approximate 0.040 for the conditions outlined.

44. Procedure

44.1 Adjust the chromatograph to the following conditions:

Chart speed, in./h	30
Column temperature, °C	100
Detector block temperature, °C	275
Gas flows, mL/min:	
Air	Note 13
Helium	40
Hydrogen	Note 13
Injection port temperature,° C	275
Sensitivity	max

NOTE 15—Adjust air-hydrogen ratio to give maximum detector sensitivity. See the Instrument Instruction Manual.

44.2 Add about 20 mL of sample to be tested to a clean, dry, 25-mL, glass-stoppered, volumetric flask, Using a 100-µL syringe, inject 100 µL of internal standard solution just below the surface of the liquid in the flask. Bring the flask to volume with sample, stopper, and mix thoroughly by shaking.

44.3 Rinse a clean, dry, 50-µL syringe several times with the sample from the flask and fill syringe to about the 25-µL mark. Inject 10 µL of sample into the chromatograph and mark the point of injection on the chart. Allow the chromatograph to proceed at attenuation settings which will keep both the ethanol and the internal standard peaks on the scale. It is not necessary to keep these peaks on the scale if electronic integration is used.

44.4 Typical retention times are as follows:

Component	Minutes
Methyl acetate	3.6
Methyl formate	3.6
Acetone	4.8
Isopropanol[A]	8.0 (internal standard)
Isobutanol[A]	9.2
n-Butanol[A]	11.0
n-Propanol[A]	11.0
Ethanol	12.4

Methanol drives pen off scale at about 14 min.

[A] Normally not found in refined methanol. Under the conditions of this test the sorbitol column will be clear after 60 min.

45. Calculation

45.1 Remove the chromatogram from the instrument and draw in the baseline of the internal standard solution and ethanol peaks.

NOTE 16—The position of a baseline is normally described as the position the recorded line would have drawn at the attenuation of the peak being measured had that peak been absent. Under ideal conditions, where the peak returns to baseline, the position of the baseline for any peak is obvious. For practical purposes, as in this method where the concentration of the compound being measured is of low order, it is satisfactory to connect the two minima of the peak even though the peak does not return to the initial baseline (Fig. 1).

45.2 Measure to the nearest 0.1 mm the height of each peak and record these heights on the chromatogram. Mark the midpoint of the peak height under each curve. Measure to the nearest 0.1 mm the width of each peak at its half-peak height and record values on the chromatogram.

NOTE 17—Alternatively, electronic integration may be used to measure the areas under the ethanol and methanol peaks.

45.3 Calculate and record the area of each peak as:

$$\text{Area, mm}^2 = XYZ \quad (4)$$

where:
X = peak height,
Y = peak width, and
Z = attenuator setting.

45.4 Calculate the peak area ratio as:

$$r = \frac{\text{area of ethanol peak}}{\text{area of Internal Standard peak}} \quad (5)$$

45.5 Divide this ratio by the calibration factor, m (see 43.7); the result is ppm ethanol, or

$$\text{Ethanol, ppm} = \frac{r}{m} \quad (6)$$

46. Report

46.1 For samples containing ethanol at the 30 ppm level,

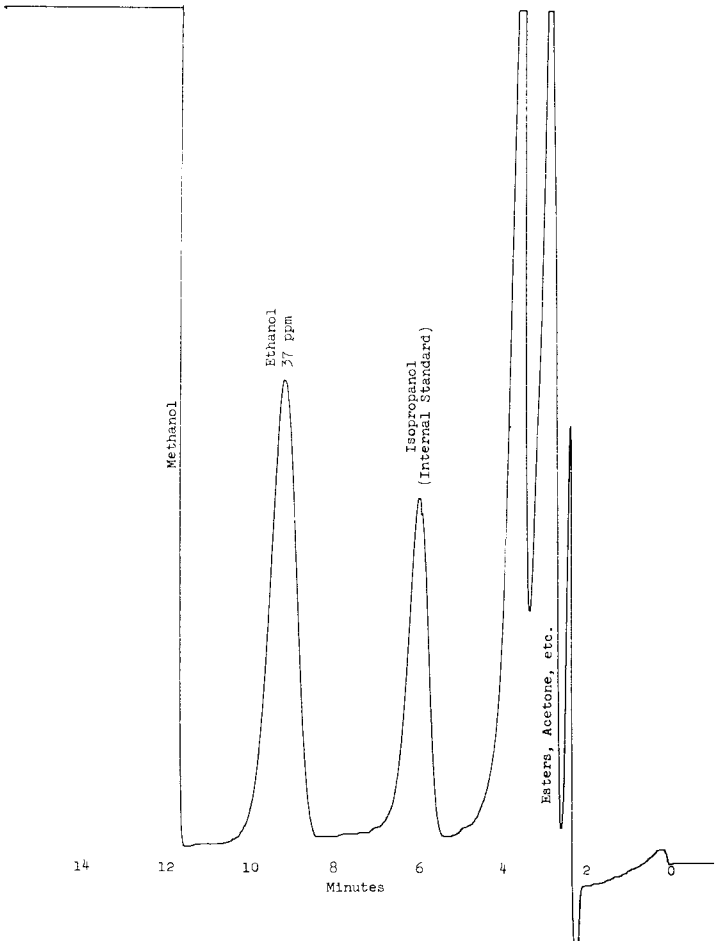

FIG. 1 Chromatogram for Refined Methanol

report the concentration to the nearest 1 ppm. For samples at the 600 ppm level, report the concentration to the nearest 10 ppm.

47. Precision and Bias

47.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 18):

47.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

47.1.2 *Laboratory Precision (Within-Lab Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

47.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 18—The above precision estimates are based on interlaboratory studies performed on two samples of methanol containing approximately 30 and 600 ppm ethanol. A total of nine laboratories cooperated in the studies in which duplicate runs were performed on each of two days. Practice E 180 was used in developing these precision estimates.

47.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

ACETONE

48. Scope

48.1 This test method covers a procedure for detecting the

TABLE 6 Ethanol Precision Values, ppm

Level, ppm	Repeatability			Laboratory Precision Within-Lab, Between-Days			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
30	1.0	18	3	1.6	8	4	4.8	7	13
600	13.5	18	38	18.9	8	53	56.4	7	158

presence of acetone in methyl alcohol (methanol) in amounts greater than 0.003 weight %.

49. Summary of Test Method

49.1 The sample is reacted with Nessler's reagent and the turbidity that is produced is compared to a standard containing the equivalent of 0.003 weight % of acetone.

50. Significance and Use

50.1 Because this test method measures trace levels of acetone, care should be taken to perform the test in an environment free of acetone, other aldehydes, ketones, and ammonia. These compounds may interfere with this test by forming turbidity or color, or both, with the reagent. Do not use acetone in cleaning or drying the glassware.

51. Apparatus

51.1 *Volumetric Pipets*, 1, 4, and 5-mL capacity.
51.2 *Test Tubes*, matched for color, 1.5 by 15 cm.

52. Reagents

52.1 *Acetone, Standard*—Pipet 6.0 mL of acetone into a 1-L volumetric flask and dilute with water to the 1-L mark. Take 1.0 mL of the resulting solution and make up to 1 L with water in a volumetric flask. Five millilitres of this solution contain 0.024 mg of acetone. Under conditions outlined for this test, the standard made up for comparison is equivalent to a methyl alcohol sample containing 0.003 weight % of acetone.

52.2 *Nessler's Reagent:*

52.2.1 *Solution A*—Dissolve 270 g of sodium hydroxide (NaOH) pellets in water and dilute to 1 L.

52.2.2 *Solution B*—Dissolve 36 g of potassium iodide (KI) crystals and 13.6 g of mercuric chloride ($HgCl_2$) powder in water and dilute to 500 mL. To prepare the Nessler's reagent, mix three parts of Solution A with 5 parts of Solution B. It should be allowed to stand until the solution is clear before using.

NOTE 19—**Caution:** Solution B and the Nessler's reagent are highly toxic.

53. Procedure

53.1 Carefully pipet 1 mL of the sample and 4 mL of water into one of the matched test tubes and mix thoroughly. Carefully pipet 5 mL of the acetone standard into a second matched test tube. Pipet 5 mL of the Nessler's reagent into each of the tubes containing the sample and the acetone standard. Quickly mix the contents of each tube and allow both to stand for 5 min. At the end of the 5-min standing period, compare the turbidity of the sample to the turbidity of the acetone standard.

54. Report

54.1 If the turbidity of the sample is less than that of the acetone standard report the acetone content as "less than 0.003 weight %." If the turbidity of the sample is greater than that of the acetone standard, report the acetone content as "greater than 0.003 weight %."

55. Precision and Bias

55.1 Because of the go, no-go nature of this test method, no precision and bias data have been obtained.

TRIMETHYLAMINE

56. Scope

56.1 This test method is used to determine the trimethylamine (TMA) content of refined methanol in the range of 10 to 100 µg/kg.

56.2 The odor of methanol has been determined to be caused primarily by the impurity TMA. The determination of TMA and its relationship to odor will eliminate the need to sniff methanol to determined odor, avoiding exposure to this toxic chemical. Although TMA has been identified as the principal cause of odor, other compounds (amines, ethers) may contribute to odor.

57. Summary of Test Method

57.1 A representative sample of methanol is introduced in a gas chromatograph equipped with a capillary column and a nitrogen phosporous detector (NPD). The TMA and the internal standard (acetonitrile or other suitable known nitrogen containing compound) are separated from the methanol and the chromatographic area of the TMA is compared to that of the internal standard. From the relative response factor of the TMA and the added internal standard, the concentration of TMA is calculated.

58. Significance and Use

58.1 This test method is designed to determine the manufacturing impurity causing odor in refined methanol. It has been determined that TMA is the primary cause of odor of methanol and it has been shown that methanol containing up to 30 µg/kg of TMA in methanol will be odor free. Methanol containing TMA at a level equal to or greater than 40 µg/kg will have detectable odor.

59. Apparatus

59.1 *Capillary Gas Chromatograph*—any gas chromatograph equipped with a nitrogen-phosphorous detector and a split injection system for use with capillary columns that can be operated at the conditions given in Table 7.

59.2 *Chromatographic Column*—The column must give satisfactory resolution and proper peak shapes for both TMA and the internal standard. A 30-m capillary column (0.53 mm inside diameter) with a 0.5-µm polyethylene glycol film (DB Wax) column has been found to be satisfactory.[8]

59.3 *Recorder/Integrator*—Electronic integration is recommended for this analysis.

59.4 *Syringe*—5 µL, 50 µL capacity.

59.5 *Injector*—An automatic injector is recommended.

60. Reagents and Materials

60.1 *Carrier Gas*—Helium, minimum purity 99.995 mol %.

60.2 *Hydrogen*—High purity.

60.3 *Air*—High purity.

[8] Polyethylene glycol phase - fused silica (DB WAX) from J & W Scientific Inc., 91 Blue Ravine Road, Folsom, CA 95630.

TABLE 7 Typical Instrument Parameters

Instrument	Parameters
Detector	Nitrogen phosphorus (thermionic specific detector)[A,B]
Column:	
Length	30 m
Inside diameter	0.53 mm
Stationary phase	DB Wax
Support	fused silica
Film thickness	0.5 µm
Temperature, °C	
Injector	250
Detector	300
Oven	45
Carrier gas	helium
Column flow	2.5 mL/min
Total flow	50 mL/min
Total chromatograph run time	11 min
Internal standard:	acetonitrile
Sample size (µL)	2.0 µL
Split ratio	1:20

[A]Refer to Practice E 1140.
[B]An HP 6390 GC was used in the development of this test method. Optimize the detector in accordance with manufacturer's recommendations.

60.4 *Methanol*—Anhydrous, chromatographic grade, shown to be free of compounds interfering with TMA or the internal standard.

NOTE 20—High purity methanol can be obtained by fractional distillation (see 41.3).

60.5 *Internal Standard*—Acetonitrile, 99.0 % minimum purity or other compounds that can be used as an internal standard, previously analyzed and found to be free of a compound interfering with TMA quantitation.

60.6 *Trimethylamine hydrochloride*—trimethylammonium chloride, 98.0 % minimum purity.

61. Calibration and Standardization

61.1 Weigh 1.28 ± 0.02 g of trimethylammonium chloride into a 1000–mL volumetric flask and dilute to volume with water. Mix well. This solution is a stock solution of 792 mg/L TMA in water.

61.1.1 Pipet 1.0 mL of the 792 mg/mL TMA solution (see 61.1) into a 1000-mL volumetric flask containing TMA free methanol. Dilute to volume with the methanol and mix well. This is a working stock solution of 1000 µg/kg TMA in methanol. If kept refrigerated this solution is stable for six months.

61.1.2 Pipet 10.0 mL of the 1000 µg/kg TMA solution (see 61.1.1) into a 100-mL volumetric flask and make to volume with methanol. This is a 100 µg/kg TMA calibration standard.

61.2 Pipet 1.0 mL of acetonitrile into a 100-mL volumetric flask about three-fourths full of methanol, dilute to the mark and mix well. This is a 7860 mg/L acetonitrile working internal standard solution.

61.3 Into each of six clean, dry, 100-mL volumetric flasks add the following volumes of the TMA calibration standard (see 61.1.2) solution: 0.0, 10.0, 20.0, 50.0 and 75.0 mL. Bring each flask to volume with TMA-free methanol, stopper each, and mix thoroughly. Using the 50-µL syringe, add 50 µL of the working internal standard solution prepared in 61.2.

61.4 The flask containing 0.0 mL of standard TMA solution will serve as a blank of the TMA free methanol. It is essential, therefore, that the same methanol be used in preparing the calibration standards.

61.5 Calculate the TMA, µg/kg, in each standard from the following:

$$TMA = \frac{B \times C}{100} \tag{7}$$

where:
B = volume of TMA standard solution, mL,
C = concentration of TMA in standard solution, µg/kg, and
100 = total volume, mL.

61.6 Calculate the response factor, *Ri*, as follows:

61.6.1 Obtain a chromatogram of each of the five TMA standards by injecting 2.0 µL or an appropriate amount of standard into the chromatograph and obtain the chromatogram. Approximate retention times for TMA is 3.22 min and 8.75 min for acetonitrile. A typical chromatogram is shown in Fig. 2.

61.6.2 Determine the area of the TMA and acetonitrile peaks.

61.6.3 Calculate the ratio *r* for each standard, after correcting for the blank, as follows

$$r = \frac{\text{area of TMA peak}}{\text{area of internal standard peak}} \tag{8}$$

:

61.6.4 Plot the *r* values for each standard against the TMA contents to determine that the calibration curve passes through zero.

61.6.5 Calculate for each standard, the response factor, R_i, for TMA relative to the internl standard after correcting for the blank as follows:

$$R_i = \frac{A_s \times F_s \times W_i}{A_i \times F_i \times W_s} \tag{9}$$

where:
R_i = response factor of TMA relative to internal standard,
A_s = area of internal standard peak,
A_i = area of TMA peak,
F_s = attenuation factor standard peak,
F_i = attenuation factor for TMA peak,
W_s = concentration internal standard, µg/kg, and
W_i = concentration TMA in synthetic standard, µg/kg.

Average the *Ri* values.

NOTE 21—If an electronic integrator is used *Fs* and *Fi* are usually 1.00.

62. Sample Analysis Procedure

62.1 Establish stable instrument operation at the prescribed (Table 7) or selected operating conditions. Reference should be made to the instructions provided by the manufacturer of the chromatograph.

62.2 Fill a clean and dry 100-mL volumetric flask with sample and add 50 µL of the internal standard solution (see 61.2), cap and mix well. If acetonitrile is used as the internal standard, this solution will contain 3.93 µg/mL acetonitrile.

62.3 Inject 2.0 µL or an appropriate amount of sample into the chromatograph and obtain the chromatogram. Approximate retention times for TMA in 3.22 min and 8.75 min for

Quantitation Report

Data File : C:\HPCHEM\1\DATA\TMA00022.D Vial: 1
Acq On : 4-4-97 10:39:28 AM Operator: JEM
Sample : TMA Std 1206-122-2 1.02ug/ml 2 ul Inst : GC Instru
Misc : Spiked with 3.1ug/ml acetonitrile Multiplr: 1.26
IntFile : autoint1.e
Quant Time: Apr 10 7:31 1997 Quant Results File: NPD.RES

Quant Method : C:\HPCHEM\1\METHODS\NPD.M (Chemstation Integrator)
Title : TMA in Methanol
Last Update : Thu Mar 27 15:57:24 1997
Response via : Multiple Level Calibration
DataAcq Meth : NPD.M

Volume Inj. :
Signal Phase :
Signal Info :

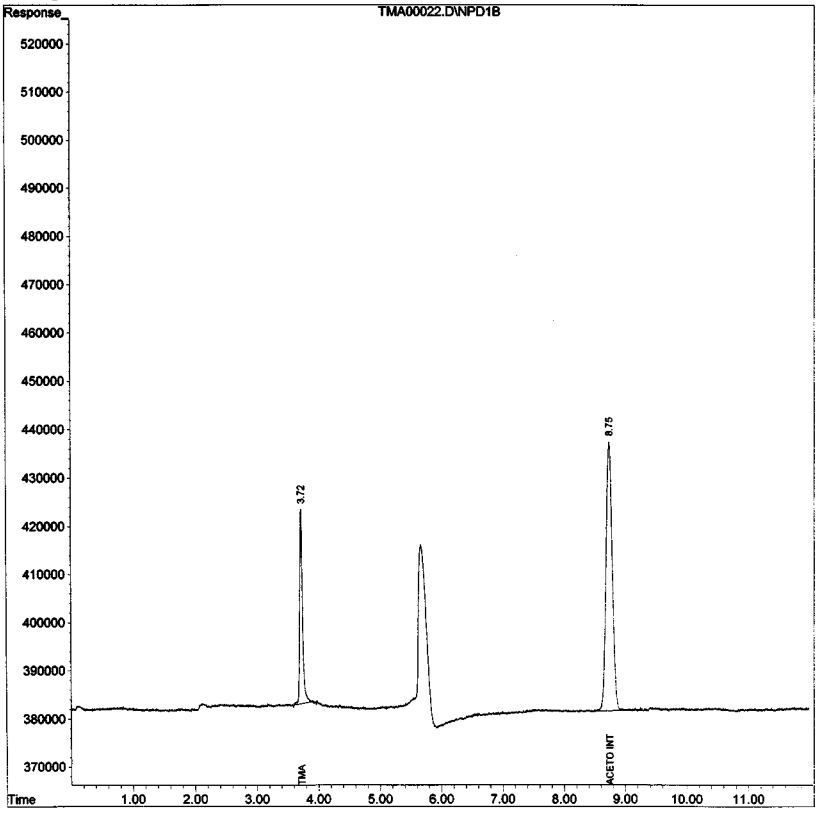

FIG. 2 Typical Chromatogram

acetonitrile. A typical chromatogram is shown in Fig. 2.

NOTE 22—A chromatogram of a TMA standard solution is used to show the TMA peak which is small in odor-free methanol.

63. Calculation

63.1 Measure the areas of the TMA and acetonitrile (internal standard) peaks.

63.2 Calculate the concentration of TMA, µg/kg, as follows: (see Note 21):

$$TMA = \frac{A_i \times R_i \times F_i \times C_s}{A_s \times F_s} \quad (10)$$

where:
A_i = area of TMA peak,
A_s = area of internal standard,
R_i = response factor TMA, relative to internal standard (average),
C_s = concentration of internal standard, µg/kg,
F_i = attenuation factor TMA, and
F_s = attenuation factor acetonitrile.

64. Report

64.1 Report results less than 10 µg/kg to one significant figure. Report results greater than 10 µg/kg to two significant figures.

65. Precision and Bias

65.1 *Precision*—The following criteria should be used to judge the acceptability of results (see Note 23):

65.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 1.35 µg/kg absolute at 10 degrees of freedom. The 95 % confidence limit for the difference between two such runs is 3.78 µg/kg.

65.1.2 The reproducibility of this test method has not been determined.

65.2 *Bias*—The bias of this test method has not been

determined due to the unavailability of suitable reference materials.

NOTE 23—The precision statements are preliminary based on 10 duplicate analyses by one analyst on one day of one sample of methanol containing approximately 30 µg/kg TMA.

66. Keywords

66.1 acetone; acidity; carbonizables; distillation range; ethanol; gas chromatography; methanol; permanganate time; specific gravity; trimethylamine; water; water miscibility