Designation: E 346 – 08

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:

	Sections
Purity of Reagents	4
Safety Precautions	5
Sampling	6
Acidity	7 to 9
Carbonizables	10 to 18
Color	19 to 21
Distillation Range	22 to 24
Permanganate Time	25 to 27
Specific Gravity	28 to 30
Water	31 to 33
Water Miscibility	34 to 37
Ethanol	37 to 47
Acetone	48 to 55
Trimethylamine	56 to 65

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

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures and safety precautions for the chemicals used in this standard.

1.4 *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 16.1, 16.4, and 52.2.2.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D 1078 Test Method for Distillation Range of Volatile Organic Liquids

D 1193 Specification for Reagent Water

F 1209 Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Ponds and Sloughs

D 1363 Test Method for Permanganate Time of Acetone and Methanol

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

D 1722 Test Method for Water Miscibility of Water-Soluble Solvents

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E 203 Test Method for Water Using Volumetric Karl Fischer Titration

E 300 Practice for Sampling Industrial Chemicals

E 1140 Practice for Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use In Gas Chromatography

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.

[1] These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.02 on Product Standards.

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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.**

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.[3] 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. 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 % mass (m/m) level, report the results to the nearest 0.0001 % mass (m/m). For concentrations at the 0.010 % masss (m/m) level, report the results to the nearest 0.001 % mass (m/m).

[3] *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.

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 % mass (m/m) 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

TABLE 1 Acidity Precision Values, % Acetic Acid

Level,% mass (m/m)	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

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.

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. (**Warning**—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. (**Warning**—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 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 3):
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 3—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 4):

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