ASTM INTERNATIONAL

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Standard Test Methods for
Analysis of Methanol[1]

This standard is issued under the fixed designation E346; 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 U.S. Department of Defense.

ε[1] NOTE—Section 2.1 Referenced Documents was editorially corrected in June 2014.

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
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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 36
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]

D891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals

D1078 Test Method for Distillation Range of Volatile Organic Liquids

D1193 Specification for Reagent Water

D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D1363 Test Method for Permanganate Time of Acetone and Methanol

D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D1722 Test Method for Water Miscibility of Water-Soluble Solvents

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E300 Practice for Sampling Industrial Chemicals

E1140 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,

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

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.[4] 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 D1193. 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 E300.

ACIDITY

7. Procedure

7.1 Determine the acidity of the methanol as acetic acid using the titration method as described in Test Method D1613.

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[4] *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.

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).

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 E180 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 D1209).

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

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

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 D1209.

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 E180 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 D1209.

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

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):

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 4—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 E180 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.

DISTILLATION RANGE

22. Procedure

22.1 Determine the distillation range of the methanol as described in Test Method D1078. 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 D1078.

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 5):

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 5—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 E180 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 D1363.

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 6—An estimate of the total permanganate time may be made by

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

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

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 7):

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 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 7—The above precision estimates are based on an interlaboratory study (Note 8) 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 E180 was used in developing these precision estimates.

Note 8—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 D891.

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 9):

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 9—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 E180 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 E203.

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.

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

32. Report

32.1 Report the percentage of water to the nearest 0.001 weight % mass (m/m).

33. Precision and Bias

33.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 10):

33.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0035 % mass (m/m) absolute at 40 df. The 95 % limit for the difference between two such runs is 0.010 % mass (m/m) 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 % mass (m/m) absolute at 20 df. The 95 % limit for the difference between two such averages is 0.015 % mass (m/m) 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 % mass (m/m) absolute at 9 df. The 95 % limit for the difference between two such averages is 0.045 % mass (m/m) absolute.

NOTE 10—The above precision estimates are based on an interlaboratory study performed on samples containing between 0.030 and 0.100 % mass (m/m) water. One analyst in each of ten laboratories performed duplicate determinations on each of two days. Practice E180 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 D1722.

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 µg/g.

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 in outside diameter, 5 mm in inside diameter, 0.051-mm wall.

40.4 *Column,* 610 cm of the stainless steel tubing, filled with 33 weight % *D*-sorbitol on 80 to 100 mesh, acid-washed orange calcinated diatomite.[5]

40.5 *Syringes.* [6]

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 µg/g 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 11—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 µg/g ethanol. Compare the ethanol peak of the distillate with that of the solution containing 10 µg/g 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

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[5] "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.

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