Designation: E2664 – 16

# Standard Test Method for Methanol Wall Wash of Marine Vessels Handling Polyester Grade Monoethylene Glycol[1]

This standard is issued under the fixed designation E2664; 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 methanol wall wash procedure and the chemical and physical analysis of the wall wash sampling for cargo tanks of marine vessels handling polyester grade monoethylene glycol. The key sections for the wall wash procedure and test methods appear in the following order:

| | Sections |
|---|---|
| Wall Wash Procedure | 7 and 8 |
| Appearance | 9 – 11 |
| Color | 12 – 14 |
| Hydrocarbons | 15 – 17 |
| Chloride | 18 – 21 |

1.2 The values given in SI units are to be considered as the standard. No other units of measurement are included in this standard.

1.3 Review the current Safety Data Sheet (SDS) for detailed information concerning toxicity, first aid procedures and safety precautions.

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.* For specific hazard statements, see Section 6.

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

D1722 Test Method for Water Miscibility of Water-Soluble Solvents

D4176 Test Method for Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures)

D5386 Test Method for Color of Liquids Using Tristimulus Colorimetry

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E2469 Test Method for Chloride in Mono-, Di- and Triethylene Glycol by Ion Chromatography

E2680 Test Method for Appearance of Clear, Transparent Liquids (Visual Inspection Procedure)

## 3. Significance and Use

3.1 The methanol wall wash test is performed to determine the cleanliness and suitability of cargo tanks or compartments on a marine vessel prior to loading polyester grade monoethylene glycol. Polyester grade monoethylene glycol has very high quality requirements and must be handled with care, as it is adversely affected by oxygen, hydrocarbons, water and chloride. It is especially susceptible to aromatic contamination, which degrades UV transmittance. Possible sources of contamination are the prior cargoes and cleaning agents. The methanol wall wash procedure provides a representative sampling of the impurities and contamination present on the sides of the cargo tank.

3.2 The test methods used for analysis of the methanol wall wash samples are capable of determining low levels of impurities or contamination in methanol. These tests include appearance, color, hydrocarbons and chloride. The producers of polyester grade monoethylene glycol need confirmation of the cleanliness and suitability of the marine vessel's tanks prior to loading with in-specification material. Cargo tanks that do not pass the wall wash test should not be loaded.

3.3 Alternative test methods and technology for several of the methods can be found in the Appendix. The alternative test methods do not have precision data for the application of these methods in analyzing methanol. Use of these methods is optional and individuals using the alternative methods should assure themselves that the method is sufficiently precise. Precision data is only for the original test methods listed.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

***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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) 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 *High-Purity Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193. It is recommended that all water be filtered through a 0.2-µm filter.

4.3 *Methanol,* ACS reagent grade with very low concentrations of chloride.

NOTE 1—Chloride in high purity methanol used for preparation of the chloride working standards should not exceed 0.01 mg/kg. This information should be provided by the supplier or determined by the analyst before use.

## 5. Quality Control

5.1 It is recommended that a control chart for the concentration of chloride in a methanol wall wash quality control sample be established and maintained according to common guidelines.[5] Measure the control sample each time a test sample(s) is tested. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests.

## 6. Hazards

6.1 Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. Sources of information include: operation manuals, SDS, literature, and other related data. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

6.2 Methanol is a flammable and toxic substance. Methanol is absorbed through the skin and by breathing the vapors. Be careful when handling a flammable solvent and work in a well-ventilated area away from sources of ignition. Use the proper Personal Protective Equipment (PPE) to minimize exposure.

[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. (USP), Rockville, MD.

[5] ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Services MNL 7A (revision of Special Technical Publication (STP) 15D).

## METHANOL WALL WASH

## 7. Procedure

7.1 All equipment must be clean and rinsed with reagent grade, low chloride methanol to prevent chloride contamination of the sample.

7.2 Pour approximately 1 L of reagent grade, low chloride methanol into a 1-L plastic squeeze bottle.

7.3 Use a plastic funnel that has been cut flat on one side to catch the methanol. The funnel and 1-L sample bottle should be rinsed with reagent grade, low chloride methanol immediately before sampling.

7.4 Clean, chemical resistant gloves and eye protection should be worn for personal protection and to prevent contamination of the samples.

7.5 Do not test wet areas of a cargo tank. The tank must be dry before conducting the wall wash tests. The tank is not acceptable for testing if wet areas are more than a few spots.

7.6 Choose two sites on each tank wall (bulkhead) approximately 15 to 20 cm wide and as high as possible (approximately 2 m high). Start spraying methanol on the wall with the spray bottle approximately 15 cm from the wall. Collect the methanol with the special funnel into a clean 1-L glass bottle with the funnel placed at least 0.3 to 0.6 m below the spray. Continue spraying methanol while moving down the wall until approximately 0.6 m from the bottom. Use approximately 200 mL of methanol on each of the four sides of the tank. Be consistent with the spraying and collecting of the methanol. Do not scrap the tank wall with the funnel when collecting the methanol.

7.7 Include “non-typical” areas, such as discolored patches, lining breaks and exposed metal. If the “non-typical” areas are less than 20 % of the tank surface, include them in the four areas normally tested. If they are more than 20 % of the tank surface, test them separately.

7.8 Test separately any areas having crystalline deposits.

7.9 Collect the methanol from the four sides of a tank into the same sample bottle. Cap the bottle, label from which cargo tank it was taken and transport to the laboratory for analysis.

7.10 Include a sample of the methanol used in the wall wash procedure. This is the analytical “blank”. This methanol will be analyzed with the tank samples and the results of the “blank” will be subtracted from each tank’s wall wash sample’s results.

## 8. Analysis

8.1 The methanol wall wash samples shall be analyzed for the following:

| | |
|---|---|
| 1. Appearance | Clear and bright (pass) |
| 2. Color | 10 Pt/Co, maximum |
| 3. Hydrocarbons | None by test (pass) |
| 4. Chloride | 0.5 mg/kg, maximum |

8.2 If the container needs to be cleaned further, a sample of the water used to do the cleaning may be sampled for chlorides. The water should contain less than 0.2 mg/kg chlorides.

## APPEARANCE

### 9. Procedure

9.1 Determine the appearance of the sample in accordance with Test Method E2680 for visual clarity and particulate contamination.

9.2 Allow the sample to equilibrate to room temperature (or to the storage temperature or the temperature at which the sample is used) prior to visual inspection. A temperature-controlled water bath can be used to bring the sample to the desired temperature if measurements must be made at a specific temperature according to product specifications.

9.3 When using a water bath, replace the sample container's cap with an airtight closure through which a calibrated temperature-sensing device is immersed in the sample. Periodically agitate the sample in a manner sufficient to homogenzide the bulk of the sample. Remove the sample container from the water bath and wipe dry. Remove the temperature-sensing device and replace the original cap before proceeding with the visual inspection.

9.4 Hold the sample up to a bright light source and visually examine the sample at arm's length for clarity, suspended matter (any foreign matter that does not float or settle to the bottom of the bottle) and any free water (or oil) droplets or layers.

9.5 Swirl the sample gently to form a vortex and avoid formation of bubbles. Examine the bottom of the vortex at arm's length for particulate matter (any foreign material that settles to the bottom of the bottle) and free water (or oil).

### 10. Report

10.1 Report the following information:

10.1.1 Report the appearance as "Pass" if the visual clarity was found to be "Clear and Bright" with no more than the maximum number of particles of suspended matter no greater than 1 mm in diameter and no free water (or oil) were found and the particulate matter had no particulates of sufficient size and quantity to be easily noted at the bottom of the vortex. See Table 1.

10.1.2 Report the appearance as "Fail" if the visual clarity as found to be "Not Clear and Bright" with more than the maximum number of particles of suspended matter greater than 1 mm in diameter and/or free water (or oil) were found and/or particulate matter was found with particulates of sufficient size and quantity to be easily noted at the bottom of the vortex. See Table 1.

**TABLE 1 Recommended Maximum Number of Suspended Particles Allowed for a Sample to Pass**

| Sample Type | Recommended Number of Particles Allowed | Typical Sample Volume (mL) |
|---|---|---|
| Methanol Wall Wash | 0 – 20 | 400 |

### 11. Precision and Bias

11.1 No information is presented about either the precision or bias of Test Method E2680 since the test result is nonquantitative.

## COLOR

### 12. Procedure

12.1 Determine the color of the sample in accordance with Test Method D5386 for near clear liquids using an instrument with color measurements converted to the platinum-cobalt system (Pt-Co).

### 13. Report

13.1 Report the following information:

13.1.1 Report the color for an instrumental Pt-Co measurement to the nearest whole unit.

### 14. Precision and Bias

14.1 The following criteria should be used to judge the acceptability of results (see Note 2):

14.1.1 *Repeatability (Single Analyst)*—The precision of the procedure for measuring color will be determined.

14.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The precision of the procedure for measuring color will be determined.

14.1.3 *Reproducibility (Multi-Laboratory)*—The precision of the procedure for measuring color will be determined.

NOTE 2—The equations in Practice E180 will be used in developing the precision estimates.

14.2 *Bias*—The bias of this test method cannot be determined because no referee method or reference standard is available to determine the true value.

## HYDROCARBONS

### 15. Procedure

15.1 Determine the presence of water-immiscible materials (hydrocarbons) in the sample in accordance with Test Method D1722. This is a qualitative test.

### 16. Report

16.1 Report the following information:

16.1.1 If the sample water mixture has no hydrocarbon layer and is as free of cloudiness or turbidity as the blank, report the sample as "passes" test. If any cloudiness, turbidity or a hydrocarbon layer is detected after 30 min, report as "fails" test.

### 17. Precision and Bias

17.1 No information is presented about either precision or bias of this test method since the test result is non-quantitative and is reported as pass or fail.

## CHLORIDE

### 18. Procedure

18.1 Determine the concentration of chloride in the sample in accordance with Test Method E2469 by ion chromatography (IC). An IC system with Carbonate-Based Eluent should produce a separation of chloride equivalent to or better than that shown in Fig. 1.

18.1.1 The chloride working standards should be prepared in methanol. The methanol used to prepare the chloride working standards should not exceed 0.01 mg/kg of chloride (see 4.3).

18.1.2 The methanol wall wash sample should be analyzed without dilution. It is recommended that each sample be analyzed in duplicate and the average result reported.

### 19. Report

19.1 Report the following information:

19.1.1 Report the concentration of chloride in the methanol wall wash sample to the nearest 0.01 mg/kg.

19.1.2 A correction should be made to each wall wash sample if chloride is found in the methanol analytical "blank" submitted with the samples.

### 20. Precision and Bias[6]

20.1 The following criteria should be used to judge the acceptability of results (see Note 3):

20.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value given in Table 2 at the indicated degrees of freedom. The 95 % limit of difference between two such runs is also given in Table 2.

**TABLE 2 Precision for Chloride in Methanol**

| Level (mg/kg) | Standard Deviation (mg/kg) | Degrees of Freedom | 95 % Range (mg/kg absolute) |
|---|---|---|---|
| IC System with Bottled Carbonate Eluent | | | |
| 0.1 | 0.0029 | 6 | 0.0082 |
| 0.5 | 0.0110 | 6 | 0.0309 |

**TABLE 3 Accuracy for Chloride in Methanol**

| Sample | Concentration Level (mg/kg) | Average Recovery (%) | Range of Recoveries (%) | Standard Deviation (%) |
|---|---|---|---|---|
| IC System with Bottled Carbonate Eluent | | | | |
| Methanol | 0.1 | 96.9 | 90.2–104.5 | 3.9 |
| Methanol | 0.5 | 97.5 | 95.1–101.4 | 2.0 |

20.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The precision of the procedure for measuring chloride will be determined.

20.1.3 *Reproducibility (Multi-Laboratory)*—The precision of the procedure for measuring chloride will be determined.

NOTE 3—The precision statements are preliminary based on six analyses by one analyst on two days of two samples of methanol containing approximately 0.1 mg/kg and 0.5 mg/kg chloride. An interlaboratory study is planned for 2008/2009. The equations in Practice E180 will be used in developing the precision estimates.[7]

20.2 *Bias:*

20.2.1 The bias of this test method was determined by spiking two samples of methanol with chloride standard at the 0.1 mg/kg and 0.5 mg/kg levels and analyzing the spiked samples six times on two days. The recovery (accuracy) and standard deviation are estimated to be the values given in Table 3 based on a linear fit of the calibration curve. The bias depends upon the accuracy of the calibration, weighing of the spike and the extent of any interferences.[7]

[6] It is recommended the precision, accuracy and linearity of the test method be verified if another set of equipment is to be used or the test method is to be used at another location.

[7] Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR:E15-1069.

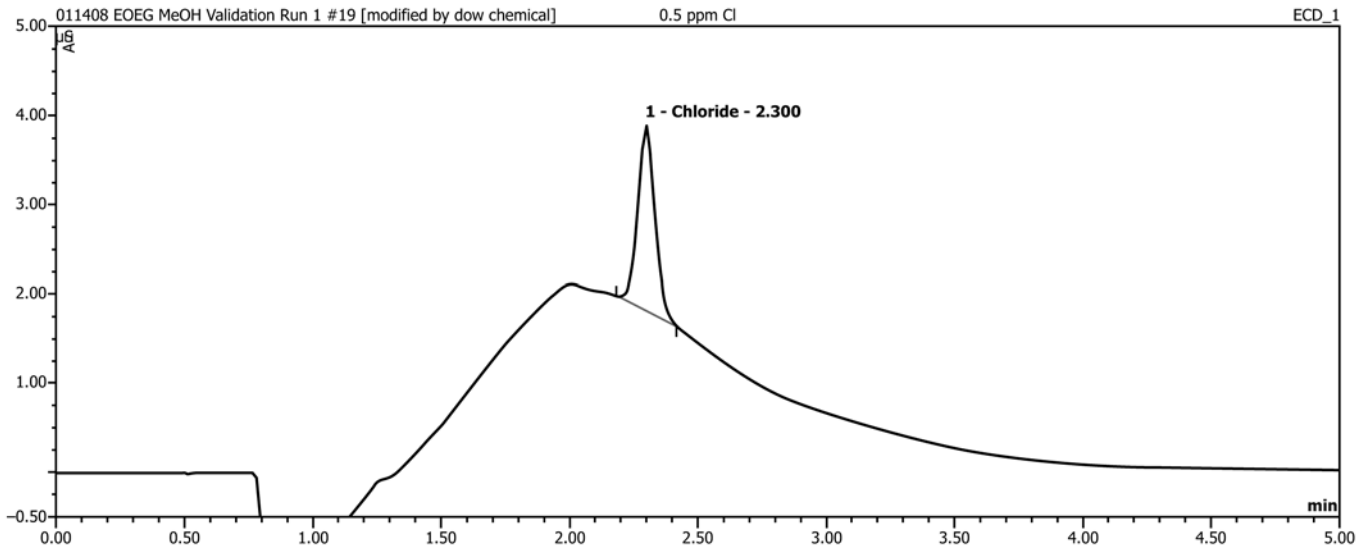


FIG. 1 0.5 mg/kg Chloride in Methanol

## 21. Linearity[6]

21.1 Peak area response for chloride was found to be linear for the Bottled Carbonate Eluent over the range of 0.01 to 1.0 mg/kg.[7]

## 22. Keywords

22.1 appearance; chloride; color; hydrocarbons; methanol; polyester grade monoethylene glycol; wall wash

# APPENDIX

## X1. ALTERNATIVE TEST METHODS

X1.1 *Scope*—Listed in Table X1.1 are alternative test methods and technology for several of the test methods. The alternative test methods do not have precision data for the application of these methods in analyzing methanol. Use of these methods is optional and individuals using the alternative methods should assure themselves that the method is sufficiently precise. Precision data presented is only for the original test methods listed.

**TABLE X1.1 Alternative Test Methods**

| Analysis | Listed Test Method | Alternative Test Method (see 3.3) |
|---|---|---|
| Appearance | E2680 | D4176 |
| Color | D5386 | D1209 |
| Hydrocarbons | D1722 | None identified |
| Chloride | E2469 | None identified |

## SUMMARY OF CHANGES

Subcommittee E15.02 has identified the location of selected changes to this standard since the last issue (E2644-09a) that may impact the use of this standard.

*(1)* 7.6 and 8.1 were revised.

*(2)* 8.2 was deleted and subsequent section was renumbered.