



Standard Test Method for Aldehydes in Mono-, Di-, and Triethylene Glycol (Spectrophotometric Method)¹

This standard is issued under the fixed designation E 2313; 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 describes the spectrophotometric determination of total aldehyde carbonyl content in the range of 0.5 to 50 mg/kg (as acetaldehyde) or 0.3 to 35 mg/kg (as formaldehyde) in mono-, di-, and triethylene glycol (MEG, DEG and TEG). Alkoxyalcohols (hemiacetals), if present, are co-determined, whereas dialkoxyalkanes (acetals), if present, are not. The results provide a measure of the purity of the sample with respect to total aldehyde carbonyl content.

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.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

D 2194 Test Method for Concentration of Formaldehyde Solutions

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

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers

E 288 Specification for Laboratory Glass Volumetric Flasks

E 300 Practice for Sampling Industrial Chemicals

¹ This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is 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.

E 969 Specification for Glass Volumetric (Transfer) Pipets

2.2 *Other Document:*

Manufacturer's Instruction Manual of Spectrophotometer

3. Summary of Test Method

3.1 The total aldehyde carbonyl content of the sample is determined spectrophotometrically. The aldehydes present are reacted with excess 3-methyl-2-benzothiazolinone hydrazone (MBTH) to form azines. An aqueous solution of iron (III) chloride is added, causing the oxidation of the excess MBTH to a reactive cation, which reacts with the previously formed azines producing bluish-green cations. Acetone or methanol is added to stop the oxidation reaction, to mask the excess MBTH and to obtain a clear solution. The absorbance of the test solution is measured spectrophotometrically at 635 nm. The amount of aldehyde present in the test solution is derived from a previously prepared calibration graph. The aldehyde content of the sample, expressed as either acetaldehyde or formaldehyde, is calculated from the data obtained.

4. Significance and Use

4.1 Knowledge of the aldehyde content of Monoethylene glycol is required to establish whether the product meets the requirements of its quality specifications.

5. Apparatus

5.1 *Spectrophotometer*, suitable for measurement at a wavelength of 635 nm, provided with cells with a pathlength of 10 mm.

NOTE 1—Further information on spectrophotometers can be obtained from Practice **E 275**.

5.2 *Analytical Balance*, readable to 0.1 mg, calibrated. Calibrate and verify at regular intervals.

5.3 *Stopwatch*, measuring accuracy ± 1 s or better. Calibrate or verify at regular intervals.

5.4 *Apparatus*, as described in Test Method **D 2194**.

5.4.1 *Buret*, calibrated, 100-mL, with a 50 or 75-mL reservoir on top of a lower portion calibrated in 0.1-mL divisions. A PTFE-fluorocarbon resin stopcock is suitable for this purpose.

5.4.2 *Erlenmeyer Flask*, approximately 5-mL capacity.

5.4.3 *Vials*, specimen, short, style, approximately 5-mL capacity.

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

5.5 Glassware:

NOTE 2—In cases where volumetric glassware is to be used, it shall conform to Grade (or Class) A specifications as described in, for example, Specification E 288 for volumetric flasks, or Specification E 969 for one-mark pipettes.

5.5.1 *Graduated Pipettes*, capable of quantitatively transferring between 0.5 and 5 mL, or

5.5.2 *Volumetric Pipette*, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 mL.

5.5.3 *Volumetric Pipettes*, 25 mL.

5.5.4 *Volumetric Flasks*, 100 mL, 1 L.

5.5.5 *Brown Bottle*, 1 L, with screw cap, for storage.

6. Reagents

6.1 *Purity of Reagents*—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.

6.1.1 *Acetone (2-propanone)*, A.R. minimum purity 99.99 % (V/V). (**Warning**—Acetone is highly flammable. Keep container in a well-ventilated place. Keep away from sources of ignition. Do not breathe vapor. Take precautionary measures against static discharges.)

6.1.2 *Formaldehyde*, A.R., 36 to 40 % mass formaldehyde solution (Formalin). (**Warning**—Formaldehyde is toxic by inhalation, in contact with skin and if swallowed. Causes burns. Possible risks of irreversible effects. May cause sensitization by skin contact. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately. Use only in well ventilated areas.)

6.1.3 *Hydrochloric Acid*, A.R., concentrated [36 % mass]. (**Warning**—Hydrochloric Acid is toxic by inhalation. Causes severe burns. Keep container in a well-ventilated place. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately.)

6.1.4 *Iron (III) Chloride*, (FeCl₃·6H₂O), A.R. (**Warning**—Iron (III) Chloride causes burns. Avoid contact with skin and eyes. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Take off immediately all contaminated clothing. Wear eye/face protection. If swallowed, seek medical advice immediately and show the container or label.)

6.1.5 *Methanol*, A.R. minimum purity 99.99 % (V/V). (**Warning**—Methanol is highly flammable. Toxic by inhalation and ingestion. Keep container in a well-ventilated place. Keep

container tightly closed. Keep away from sources of ignition. Avoid contact with skin. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

6.1.6 *3-Methyl-2-Benzothiazolinone Hydrazone Hydrochloride (MBTH)*. (**Warning**—MBTH is toxic if swallowed. Irritating to eyes. Keep locked up. Avoid contact with skin and eyes. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. This material and its container must be disposed of in a safe way. Wear suitable protective clothing. In case of accident or if you feel unwell, seek medical advice immediately. If swallowed, seek medical advice immediately and show the container or label.)

6.2 *Water*, reagent water conforming to Type IV of Specification D 1193.

6.3 Solutions:

6.3.1 *Standard Formaldehyde Solution*, 8.0 µg/mL, aqueous. Determine the exact concentration (c_1) of an A.R. 36 to 40 % mass formaldehyde solution (**Warning**—See 6.1.2) according to Test Method D 2194, expressing the result in g/100 mL. Weigh approximately 2.0 to 2.2 g (m_1) of the formaldehyde solution to the nearest 0.1 mg, into a 100-mL volumetric flask. Make up to the mark with water and mix thoroughly. Pipette 1.0 mL of this solution into a 1-L volumetric flask. Make up to the mark with water and mix thoroughly. Transfer this solution to a brown bottle with screw cap. Calculate the exact formaldehyde content of this solution (c_2), in µg/mL, by means of the following equation:

$$c_2, \mu\text{g/mL} = \frac{m_1 \times c_1}{10} \quad (1)$$

where:

c_1 = concentration of concentrated formaldehyde solution used, g/100 mL, and

m_1 = mass of concentrated formaldehyde solution taken, g.

The concentrated and diluted formaldehyde solutions are stable in excess of six months if stored at room temperature. Do not store in a refrigerator. Prepare fresh solutions every six months.

6.3.2 *Hydrochloric Acid*, 50 % (V/V). Dilute one volume of A.R. concentrated hydrochloric acid (**Warning**—See 6.1.3) with one volume of water.

6.3.3 *Iron (III) Chloride Solution*, 0.3 % mass, aqueous. Dissolve 5 g of A.R. iron (III) chloride. 6H₂O (**Warning**—See 6.1.4) in water, adding 1 or 2 drops of A.R. concentrated hydrochloric acid to stabilize solution (**Warning**—See 6.1.3) and dilute to 1 L with water. Prepare a fresh solution daily.

6.3.4 *Methyl-2-benzothiazolone Hydrazone Solution (MBTH solution)*, 0.4 % mass, aqueous. Dissolve 400 ± 1 mg of MBTH hydrochloride (**Warning**—See 6.1.6) in water in a 100-mL volumetric flask. Make up to the mark and mix thoroughly. Prepare a fresh solution daily.

6.4 *Reagents*, as described in Test Method D 2194, for the standardization of formaldehyde solution (see 6.3.1).

6.4.1 *Sodium Sulfite Solution*, 12.5 % mass, aqueous. Dissolve 125 g of anhydrous sodium sulfite (Na₂SO₃) in water and dilute to 1 L.

NOTE 3—Sodium sulfite gradually oxidizes to sodium sulfate on

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 *Annual 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.

exposure to air and therefore should be kept in a tightly closed container. For best results freshly prepared reagent should be used.

6.4.2 *Sulfuric Acid*, 0.5 mol/m³ (1.0 N). Prepare and standardize sulfuric acid (H₂SO₄) against 0.5 mol/m³ (0.5 N) sodium hydroxide (NaOH) solution which has been standardized against potassium acid phthalate to a thymolphthalein end point.

6.4.3 *Thymolphthalein Indicator*, 0.1 % mass, alcohol solution. Dissolve 1.0 g of thymolphthalein in 100 mL of methanol, ethanol, or isopropanol and dilute to 1 L with additional alcohol.

6.5 *Ethylene Glycol Quality Control Sample*—Fiber grade MEG, DEG or TEG (only required if maintaining a control chart, see 10.9). Store at a temperature between 0 and 5°C. Warm to ambient temperature before use.

7. Sampling, Test Specimens, and Test Units

7.1 Follow the relevant instructions for sampling as given in Practice E 300.

8. Preparation of Apparatus

8.1 *Spectrophotometer*—Check the performance of the spectrophotometer at regular intervals according to the guidelines given in Practice E 275 and the manufacturer's instruction manual.

8.2 *Glassware*—Thoroughly clean the cells and other glassware using 50 % (V/V) hydrochloric acid (**Warning**—See 6.1.3) according to the guidelines in Practice E 275. If the glassware is persistently stained by iron (III) chloride, clean the affected glassware in a concentrated hydrochloric acid bath. Do not use acetone for cleaning, since this reacts with MBTH.

9. Calibration

9.1 Introduce the amounts of reagents as listed in Table 1 into separate 100-mL volumetric flasks (see 8.2) in the following way: First introduce the standard formaldehyde solution and water by means of a pipette, followed by MBTH solution.

9.2 Proceed as described in 10.6 through 10.8, measuring the absorbances of the calibration solutions, including the blank solutions, against water at 635 nm in a 10-mm cell.

9.3 Correct the absorbances measured for the calibration solutions by subtracting the mean absorbance found for the three blank solutions. If the mean blank absorbance exceeds its upper control limit, the glassware must be cleaned and the calibration repeated (see 10.9).

TABLE 1 Amounts of Reagents to be Added to the Calibration Solutions

Calibration Solution, No.	Standard Formaldehyde Solution, mL	Water, mL	MBTH Solution, mL
Blank 1	0.0	5.0	5.0
Blank 2	0.0	5.0	5.0
Blank 3	0.0	5.0	5.0
1	0.5	4.5	5.0
2	1.0	4.0	5.0
3	2.0	3.0	5.0
4	3.0	2.0	5.0
5	4.0	1.0	5.0
6	5.0	0.0	5.0

9.4 Calculate the exact amount, in µg, of formaldehyde present in each of the 7 calibration solutions, which will be in the order of 0.0, 4.0, 8.0, 16.0, 24.0, 32.0 and 40.0 µg.

9.5 Construct a calibration graph by plotting the corrected absorbances against the corresponding amount of formaldehyde in each calibration solution. Apply simple linear regression to obtain the best straight line (calibration function).

NOTE 4—Many spectrophotometers have the ability to calculate a calibration graph automatically after measuring the calibration solutions and subsequently to show the amount/concentration of the component being measured directly on a display. In such cases, no calibration graphs need to be constructed and the calculation can be started with 11.2. It is, however, recommended to verify the calculation procedure of the instrument and to establish the characteristics of the calibration graph according to suitable regression analysis software.

NOTE 5—The entire calibration graph is based on only one starting solution. In such a case, a weighing error, for example, could introduce significant errors when reading concentrations in test solutions. It is, therefore, recommended to either:

(i) Prepare a separately weighed control solution with an accurately known amount of approximately 20 µg of formaldehyde and perform 9.2, measuring the absorbance of the control solution. Obtain the amount of formaldehyde of the control solution from the calibration graph/function. If this value and the calculated value of the control solution differ by more than 5 % of their mean, repeat the calibration.

(ii) Maintain a record or control chart of the slope of the calibration graph. If a significant difference with earlier values is obtained, repeat the calibration.

10. Procedure

10.1 Although the determination in this procedure is described such that only one test result is obtained, it is strongly recommended to perform a second (duplicate) determination to enable comparison of the duplicate results with the listed repeatability value.

10.2 Place a 100-mL volumetric flask onto the balance and tare or record the tare weight to the nearest 0.1 mg. Pipet 1 mL of sample into the flask, reweigh the flask and record the increase in weight as the mass of the sample (m₂).

10.3 Using a pipette, add 4 mL water to the sample flask to make a total volume of 5 mL in each flask.

10.4 Prepare a blank solution in the same way by taking 5 mL of water in place of the prescribed volumes of test sample and water.

10.5 Using a pipette, add 5 mL of MBTH solution (see 6.3.4) into each 100-mL flask.

10.6 Thoroughly swirl the flasks and allow to stand for 30 min at room temperature. Pipette 25 mL of iron (III) chloride solution (see 6.3.3) into each of the flasks. Again mix well by thorough swirling and allow to stand for exactly 5 min at room temperature. Make up to the mark with acetone or methanol (**Warning**—See 6.1.1 and 6.1.5) and mix thoroughly.

10.7 Measure the absorbances of the solutions relative to water, at 635 nm in a 10-mm cell.

10.8 Subtract the absorbance of the blank solution from the absorbance of each test solution. If the blank absorbance exceeds its upper control limit (see 10.9), clean the glassware and repeat the measurement of the sample solutions.

NOTE 6—Sample solutions with an absorbance reading less than 0.200 must be reanalyzed, by increasing the sample size in 10.2 to 4 mL and reducing the amount of water to 1 mL. Do not use more than 5 mL of

sample. Sample solutions reading an absorbance greater than 0.800 must be reanalyzed. Use an appropriate test portion to give an approximate reading of 0.5, and follow 10.2 through 10.8. Do not dilute with acetone (methanol) and re-measure the absorbance; absorbance does not correlate linearly with serial dilution for this technique.

10.9 Quality Control—It is recommended that a control chart for the aldehyde concentration of the glycol quality control sample be established and maintained according to generally accepted guidelines.⁴ Measure the control samples each time a test sample(s) is tested using the same calibration procedure as applied for the sample. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests. A separate control chart should be maintained for the blank solutions, measured at the same time as the control sample. Use the control chart to monitor the mean and standard deviation of the blank solutions. If an individual blank measurement falls outside the action limits of the control chart (3 standard deviations of the mean), but in no case by more than 0.07 absorbance units, acid-clean all the glassware and reanalyze the batch of samples.

11. Calculation

11.1 Correct the absorbance found for the test solutions by subtracting the mean value found for the blank solutions. From the calibration graph or calculated calibration function (9.5), obtain the amount of formaldehyde (m_3), in μg , present in the test solution.

11.2 Calculate the aldehyde content of the test sample by means of the following equations:

$$\text{Aldehyde (as formaldehyde), mg/kg} = \frac{m_3}{m_2} \quad (2)$$

$$\text{Aldehyde (as acetaldehyde), mg/kg} = \frac{44.05}{30.03} \times \frac{m_3}{m_2} \quad (3)$$

where:

m_3 = amount of formaldehyde as obtained in 11.1, μg , and

m_2 = mass of test portion from 10.2, g.

12. Report

12.1 Report the aldehyde content of the sample, expressed as acetaldehyde or formaldehyde, to the nearest 0.1 mg/kg.

13. Precision and Bias

13.1 In 2007, Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study #52 to determine precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratory study of E 2313, Standard Test Method for Aldehydes in Mono-, Di-, and Triethylene Glycol (Spectrophotometric Method). Each of seventeen laboratories were asked to test three different materials. 17 laboratories tested MEG, 13 laboratories tested DEG and 12 laboratories tested TEG. Every test result represents an individual determination. Two test results were conducted on each of two days for a total

of four test results per assay. Note that in the combined study, 8 labs used a single analyst, 7 labs used two analysts (on different days) and 2 labs did not record this information. In the event that there were missing values for one or more labs, this information was noted in the results. The details of this study are given in ASTM Research Report No. E15-1065.⁵

13.1.1 Repeatability—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the r value for that material; r is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

13.1.2 Reproducibility—Two test results shall be judged not equivalent if they differ by more than the R value for that material; R is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

13.1.3 Intermediate Precision—The day-to-day standard deviation within a laboratory for results produced by the same operator, determined through statistical analysis following Practice E 180. Practice E 180 was used to conform to this particular study design which required an estimate of intermediate precision. The statistical analysis was conducted using the SAS statistical analysis software, Version 8.0.

13.1.3.1 The E 180 analysis considers the two test results from each day as being run under repeatability conditions and estimates the repeatability, intermediate, and reproducibility precision for each assay. The repeatability precision would be estimated from the two sets of duplicate test results within each day, and the intermediate precision would be estimated from the agreement between the two days, all pooled over laboratories. Caveat: Since two days is a short time period, the intermediate precision would probably be underestimated by the E 180 analysis.

13.1.4 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

13.2 Bias—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

13.3 The precision statement was determined through statistical examination of qualified results, from seventeen laboratories, on three materials. These three materials were described as the following: Fluid 1: Monoethylene glycol. Fluid 2: Diethylene glycol. Fluid 3: Triethylene glycol. To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

14. Keywords

14.1 aldehyde; diethylene glycol; MBTH; monoethylene glycol; spectrophotometric; triethylene glycol

⁴ ASTM Manual on Presentation of Data and Control Chart Analysis: 7th edition, ASTM Manual Series MNL 7A.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E15-1065.

TABLE 2 E 2313 Aldehyde in MEG, DEG, and TEG

Test Result mg/kg	Sample	Average over all Laboratories	Repeatability Standard Deviation	Intermediate Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Intermediate Limit	Reproducibility Limit
Aldehyde	MEG	4.22	0.12	0.23	1.30	0.35	0.64	3.63
Aldehyde	DEG	29.69	0.79	1.06	11.42	2.20	2.96	31.98
Aldehyde	TEG	169.29	4.01	12.86	63.66	11.22	36.01	178.24

SUMMARY OF CHANGES

Committee E15 has identified the location of selected changes to this standard since the last issue (E 2313 – 04) that may impact the use of this standard. (Approved April 1, 2008.)

(I) Revised Precision and Bias statement.

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