Designation: D 5910 – 96

Standard Test Method for Determination of Free Formaldehyde in Emulsion Polymers by Liquid Chromatography[1]

This standard is issued under the fixed designation D 5910; 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 is used for the determination of free formaldehyde (HCHO) in emulsion polymers without upsetting existing formaldehyde equilibria. The procedure has been evaluated using acrylic, acrylonitrile-butadiene, carboxylated styrene-butadiene and polyvinyl acetate emulsion polymers. This test method may also be applicable for emulsion polymers of other compositions. The established working range of this test method is from 0.05 to 15 ppm formaldehyde. Emulsion polymers must be diluted to meet the working range.

1.2 This test method minimizes changes in free formaldehyde concentration that can result from changes in the physical or chemical properties of an emulsion polymer.

1.3 There are no known limitations to this test method when used in the manner described. The emulsion polymer test specimen must be prepared with a diluent that has a pH similar to that of the emulsion. Use of an inappropriate pH may upset formaldehyde equilibria and result in incorrect formaldehyde levels.

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:*

D 1193 Specification for Reagent Water[2]

D 2194 Test Method for Concentration of Formaldehyde Solutions[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]

E 682 Practice for Liquid Chromatography Terms and Relationships[5]

3. Summary of Test Method

3.1 The aqueous phase of an emulsion polymer is diluted and chromatographed on a reversed-phase octadecyl silane (ODS) column using an aqueous mobile phase and a visible-light detector at 410 nm. Formaldehyde is separated from other species in the matrix on a chromatographic column. The detection system includes a post-column reactor that produces a lutidine derivative when formaldehyde reacts with the 2,4-pentanedione reagent (Nash Reagent). The concentration of free formaldehyde in emulsion polymers is determined using peak areas from the standard and sample chromatograms. This test method is specific for formaldehyde.

4. Significance and Use

4.1 With the need to calculate free formaldehyde levels in emulsion polymers, it is necessary to make the determination without upsetting any equilibria that might generate or deplete formaldehyde. This test method provides a means for determining ppm levels of free formaldehyde in emulsion polymers without upsetting existing equilibria.

5. Interferences

5.1 This test method is very selective for formaldehyde. Potential interferants are either chromatographically separated from formaldehyde or do not react with the post-column reagent.

NOTE 1—The following species were identified as possible interferences for the method: acetaldehyde, acetone, benzaldehyde, formamide, formic acid, glyoxylic acid and propionaldehyde. These species, when chromatographed using this test method, did not interfere with the formaldehyde peak at the 1000 ppm level or lower.

5.2 Because emulsion polymers vary in composition, the method run time may need to be extended to allow for late eluting compounds. Compounds that remain on the column after an analysis may interfere with the formaldehyde peak in subsequent runs.

6. Apparatus

6.1 *Liquid Chromatograph*—Any liquid chromatographic instrument having an injection valve, a post-column reactor, a 410-nm UV-Vis detector, and an isocratic solvent delivery system may be used. The solvent delivery system must deliver

[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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

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

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

[5] *Annual Book of ASTM Standards*, Vol 14.01.

a mobile phase flow of 0.6 mL/min.

NOTE 2—The UV-Vis detector may incorporate either a tungsten lamp or a deuterium lamp with a second order visible filter that filters out light below 400 nm.

6.2 *Post-Column Reactor*—Any post-column reactor that can deliver a reagent flow at 0.5 mL/min, contains a *Knitted Reaction Coil*[6] that can be heated to 95°C and contains a static mixing tee.[7,8]

6.3 *Chromatographic Column*—Column should be 250 by 4.6 mm inside diameter packed with a reversed-phase pH stable C18, 5-µm particles.[9]

6.4 *Chromatographic Guard Column*—The column should be 10 by 4.6 mm inside diameter packed with a reversed-phase pH stable C18 5-µm particles.[10]

6.5 *Data System*, that can collect data at 1 point/s from a 1-V output detector.

6.6 *Syringe*—100 µL capacity.

6.7 *Sample Filter*—The filter should consist of a 5-mL sample syringe and a 0.1-µm-filter assembly to remove micro particulate matter from the prepared sample solution.[11]

6.8 *Centrifuge*—Any high speed centrifuge that can generate 50 000 r/min (274 980 g) or greater (Procedure 2).

6.9 *Centrifuge*—Any centrifuge that can generate 1000 r/min or greater (Procedure 3).

7. Configuration of Liquid Chromatograph

7.1 An in-line check valve[12] is placed between the pump and the injector. The guard and analytical columns are connected to the injector. The outlet of the analytical column is connected to the mixing tee as described in 8.1.

8. Configuration of Post-Column Reactor (PCR)

8.1 The post-column reagent passes through a pulsedampener[13] and an in-line check valve[12] prior to the mixing tee. The outlet of the analytical column is connected to one side of a mixing tee. The reaction coil is connected to the outlet of the mixing tee. Stainless steel tubing with 0.25-mm inside diameter is used to make the connections. Tubing lengths should be kept to a minimum. The mixing tee and reaction coil are placed inside a 95°C oven. A 40 cm-length of 0.25-mm inside diameter stainless steel tubing is connected to the outlet of the reaction coil and is placed in an ambient-temperature stirred water bath. (This configuration acts as a heat exchanger.) The exit of the stainless steel tubing is connected to the UV/Vis detector. Fig. 1 shows a schematic of the system.

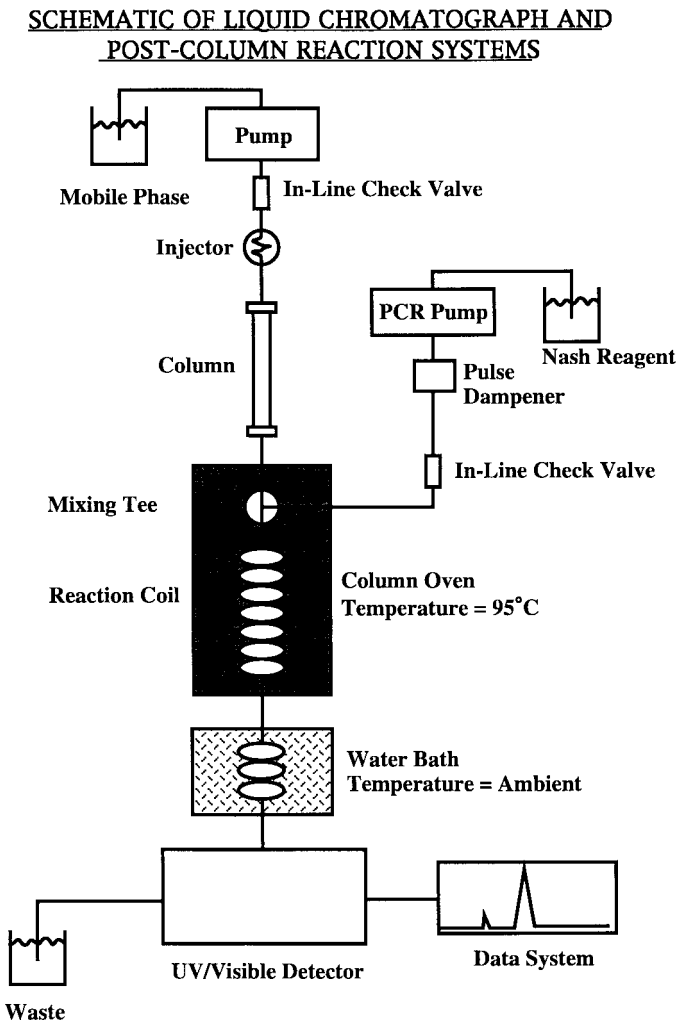

FIG. 1 Schematic of Liquid Chromatograph and Post-Column Reaction Systems

9. Reagents and Materials

9.1 *Purity of Reagents*—Reagent grade chemicals shall be used with this test method. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[14] Other grades may be used, provided it is first ascertained that the

[6] Knitted capillary delay tube such as Supelco No. 5-9206 available from Supelco Inc., Supelco Park, Bellefonte, PA 16823 has been found satisfactory for this purpose.

[7] Static mixing tee, available from Upchurch Scientific, 619 W. Oak St., P.O. Box 1529, Oak Harbor, WA 98277-1529, Catalog No. U-466, has been found to be satisfactory for this purpose.

[8] Timberline RDR-1, available from Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015, with two 0.4-mL serpentine reaction coils in series, has been found to be satisfactory for this purpose.

[9] Commercial analytical columns that have been found to be satisfactory for use during round-robin evaluation include: Phase Separations, Inc., 140 Water St., Norwalk, CT 06854, pH Stable C18, Catalog No. 838715 and Alltech Associates, Inc., Spherisorb pH Stable C18 Sil 5U, Catalog No. 82055.

[10] Commercial guard columns that have found to be satisfactory for use during round-robin evaluation include: Alltech Associates, Inc., Spherisorb pH Stable C18 Sil 5U, Catalog No. C-8800.

[11] Filter such as Anotop 25 Plus Syringe Filter, 0.1 µm, Catalog No. 2270, available from Alltech Assoc., has been found to be satisfactory for this purpose.

[12] In-line check valve CV-3001 and U-469, Catalog No. 2270, from Upchurch Scientific has been found to be satisfactory for this purpose.

[13] Pulse dampener, SSI LO, Catalog No. 20-0218, available from Alltech Assoc., has been found to be satisfactory for this purpose.

[14] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

9.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water minimally conforming to Type II of Specification D 1193, or distilled deionized water. High-performance liquid chromatography (HPLC) grade water from chromatography suppliers is also acceptable.

9.3 *Acetic Acid*, glacial (CH_3CO_2H).

9.4 *Ammonium Acetate*—($CH_3CO_2NH_4$).

9.5 *Formaldehyde*, 37 % (HCHO).

9.6 *2,4-Pentanedione*, 99 % ($CH_3COCH_2COCH_3$).[15]

9.7 *Phosphoric Acid Solution (0.1 N)*— Dissolve 2.3 mL of phosphoric acid 85 % (H_3PO_4) in water and dilute to 1 L with water.

9.8 *Potassium Ferrocyanide Trihydrate Solution (36 g/L) [Carrez Solution I]*—Dissolve 26 g of potassium ferrocyanide trihydrate, 99 % ($K_4Fe(CN)_6 \cdot 3H_2O$) in water and dilute to 1 L with water.

9.9 *Zinc Sulfate Heptahydrate (72 g/L) [Carrez Solution II]*—Dissolve 72 g of zinc sulfate heptahydrate, 99.9 % ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 L with water.

9.10 *Sodium Hydroxide (0.1 N)*—Dissolve 8 g of sodium hydroxide 50 % (NaOH) in water and dilute to 1 L with water.

9.11 *Sodium Phosphate*, dibasic, 98 % (Na_2HPO_4).

10. Preparation

10.1 *Post-Column Reagent (Nash Reagent)*:

10.1.1 Transfer 62.5 g of ammonium acetate to a 1-L amber bottle[16] that contains a stir bar. Add 600 mL of water to the bottle and mix on a stir plate until the ammonium acetate has completed dissolved.

10.1.2 Pipet 7.5 mL of glacial acetic acid into the bottle. Pipet 5 mL of 2,4-pentanedione into the bottle. Add 387.5 mL of water to the bottle and mix thoroughly (45 min of mixing is suggested).

NOTE 3—2,4-Pentanedione is light sensitive and should be protected from light during use.

NOTE 4—The post-column reagent should be prepared weekly.

10.1.3 Transfer the post-column reagent to the post-column reactor reservoir. The reservoir should be protected from light.

10.1.4 Degas the post-column reagent with a helium sparge.

10.2 *Mobile Phase and Standard Diluent*:

10.2.1 Transfer 1.78 g of sodium phosphate, dibasic to a 2-L mobile phase reservoir that contains a stir bar. Add 2 L of water and mix on a stir plate until the sodium phosphate, dibasic has completely dissolved.

10.2.2 Adjust the pH of the solution to 7.0 with 0.1 *N* phosphoric acid.

10.2.3 Degas the mobile phase with a helium sparge.

NOTE 5—Water may also be used as the mobile phase without the addition of a buffer. A water mobile phase should be used when the Carrez reagents are used in the sample preparation (see section 12.2.3).

10.3 *Sample Diluent*:

10.3.1 Transfer 0.89 g of sodium phosphate, dibasic to a 1-L bottle that contains a stir bar. Add 1 L of water and mix on a stir plate until the sodium phosphate, dibasic has completely dissolved.

10.3.2 The final step of the diluent preparation requires a pH adjustment. Before that step can occur the pH of the emulsion polymers must be measured to 0.1 pH unit. The emulsion polymers must be diluted with a buffer that is ±0.1 pH unit of the emulsion polymer.

10.3.3 Divide the 1-L solution into the number of separate diluents required as mentioned in 10.3.2.

10.3.4 Adjust the pH of the diluents to 0.1 pH unit using either 0.1 *N* NaOH or 0.1 *N* H_3PO_4.

11. Operating Conditions for Analysis

11.1 Adjust the liquid chromatograph in accordance with the manufacturers' directions and the following parameters. Allow the instrument to equilibrate until a stable base line is obtained on the data system.

Column temperature:	ambient
Mobile phase:	6.3 mM Na_2HPO_4 (pH = 7) or water
Flow rate:	0.6 mL/min
Injection volume:	50 µL
PCR temperature:	95°C
PCR flow rate:	0.5 mL/min
Detector:	UV/Vis, 410 nm

11.2 Determine whether the system is working properly by injecting 50 µL of a 10 ppm formaldehyde standard solution. A typical chromatogram of a 10-ppm formaldehyde standard obtained under the conditions outlined in 11.1 is shown in Fig. 2. Make sure that the peak asymmetry (A_s at 10 % peak height) value for formaldehyde is within the range of 0.8 and 1.7. Determination of peak asymmetry should be performed in accordance with Practice E 682. A typical retention time for formaldehyde is 6 min.

11.3 The run time for the analysis is 10 min. The run time may have to be extended 20 to 30 min if late eluting compounds interfere with the formaldehyde peak in subsequent runs.

12. Calibration and Standardization

12.1 Prepare a 25-mL stock solution of formaldehyde at the 1.18 % (11 840 ppm) level by adding 0.8 g of formaldehyde (37 %) to 24.2 g standard diluent.

NOTE 6—Reagent grade formaldehyde is nominally 37 %. Perform the assay of the formaldehyde solution in accordance with Test Method D 2194.

12.2 Calculate the formaldehyde concentration of the stock solution according to the following equation:

$$\text{Formaldehyde, ppm} = (A \times 10^3) / B \quad (1)$$

where:

A = weight of formaldehyde, mg (corrected for active ingredient), and

B = weight of formaldehyde and diluent, g.

12.3 Prepare calibration standards ranging from 0.05 to 15 ppm of formaldehyde in standard diluent.

12.4 Inject 50 µL of each standard solution and a reagent blank (standard diluent) into the liquid chromatograph.

[15] 2,4-Pentanedione (acetyl acetone), 99 %, available from Aldrich Chemical Co., 2905 W. Hope Ave., Milwaukee, WI 53216, Catalog No. P775-4, has been found to be satisfactory for this method.

[16] A bottle that filters out ultraviolet and visible light is suitable.

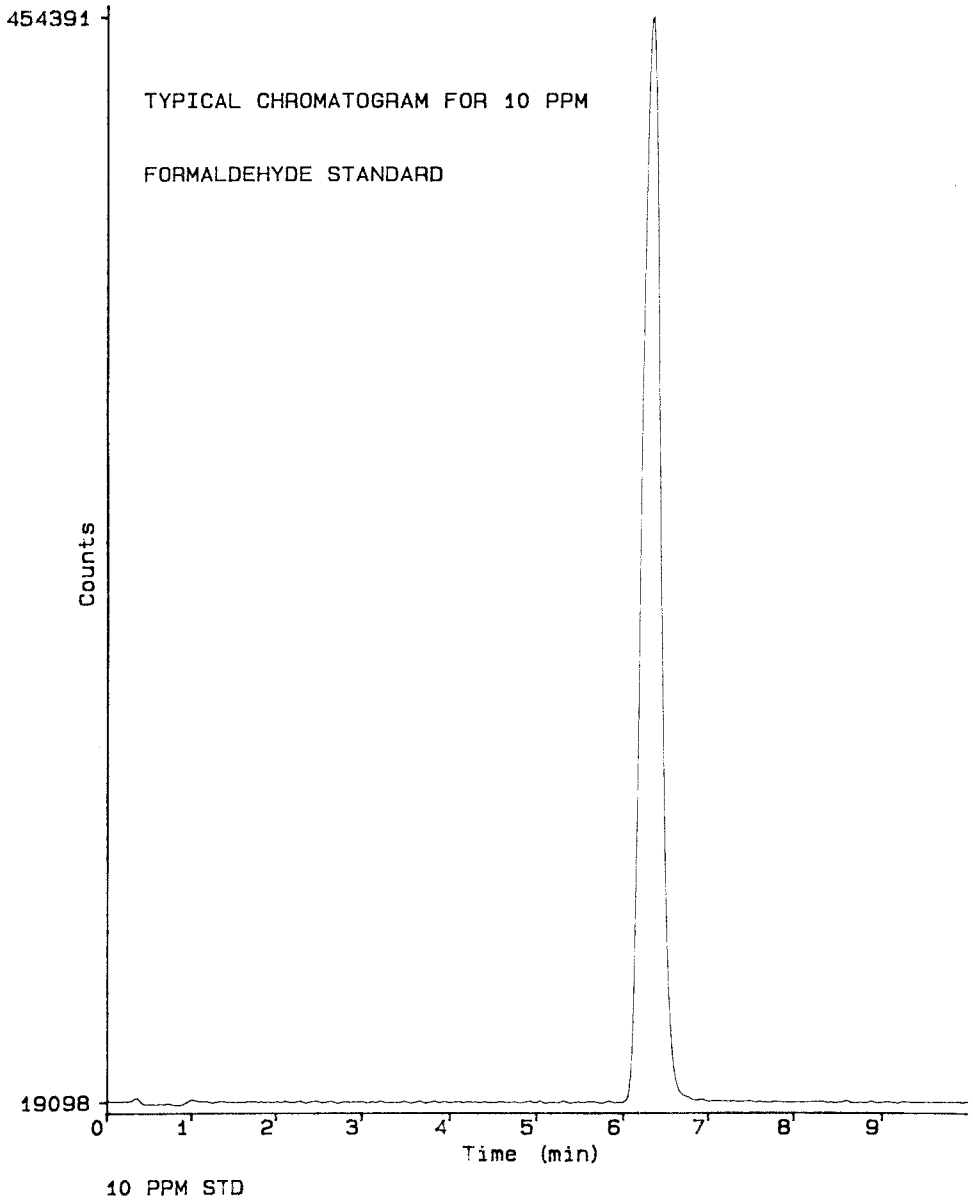

FIG. 2 Chromatogram of 10 ppm Formaldehyde Standard

NOTE 7—Store stock and standard solutions in a refrigerator when not in use. Prepare the stock and standard solutions weekly.

12.5 The area under the formaldehyde peak in the chromatogram is considered a quantitative measure of the corresponding compound.

12.6 Measure the area of the formaldehyde peak by conventional means (Note 8). Prepare a calibration curve by plotting the integrated peak area versus the concentration (ppm) of formaldehyde as in Fig. 3. The calibration must be done to ensure that the entire chromatographic system is operating properly and that the concentration of formaldehyde has not exceeded the linear response range of any part of the system; that is, column, detector, integrator, and other components. Make sure that the calibration plot is linear (Note 9).

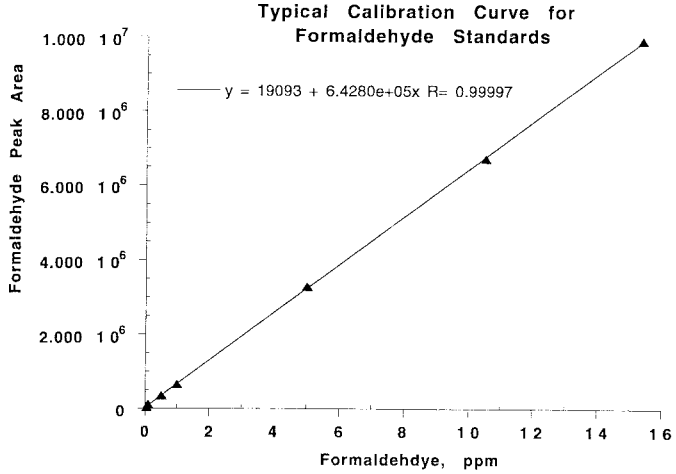

FIG. 3 Calibration Curve for Formaldehyde Standards

NOTE 8—The precision statement in Section 15 was developed from results obtained using electronic integrators or on-line computers. The precision statement may not apply if other methods of integration or peak area measurement are used.

NOTE 9—If the calibration is linear, a least-squares calculation may be performed to obtain a calibration factor. The precision statement in Section 15 was developed from calibration plots using a linear least-squares calculation and may not apply if calibration factors are used.

13. Procedure

13.1 *Preparation of Emulsion Polymer Samples*:

13.1.1 Transfer a 1-g test specimen of emulsion polymer to a vial that has previously been tared to the nearest 0.1 mg. Reweigh to 0.1 mg to determine the exact weight of the emulsion. Add 9 g of the appropriate sample diluent (see 10.3.2). Reweigh to 0.1 mg to determine the exact weight of the emulsion and the sample diluent.

13.1.2 Mix thoroughly by shaking for 1 h.

13.2 *Extraction of Emulsion Polymer*— This test method requires the analysis of a clear, particulate free, aqueous solution from the diluted emulsion polymer. Three procedures are described for treating the diluted emulsion polymer solution (13.1.1) to obtain a specimen suitable for analysis.

13.2.1 *Procedure 1 (Filtering)*—Filter the diluted solution through a 0.1 µm filter and collect the filtrate.

13.2.2 *Procedure 2 (Centrifuging)*—Centrifuge the diluted solution for 20 min at a speed greater than 50 000 r/min (274 980 g) at 20°C. Collect the supernatant.

13.2.3 Filter the supernatant through a 0.1 µm filter and collect the filtrate.

13.2.4 *Procedure 3 (Coagulating)*—Pipet 2 mL of the Carrez 1 and then 2 mL of the Carrez II reagents into the diluted solution. Shake for 30 min.

13.2.5 Centrifuge on a low speed centrifuge (1000 r/min). Collect the supernatant.

13.2.6 Filter the supernatant through a 0.1 µm filter and collect the filtrate.

NOTE 10—The filtrates can be further diluted with sample diluent if needed.

13.3 Repeat 13.1 and 13.2 with sample diluent (blank) as a method blank. One method blank will be prepared for each procedure used in 13.2.

13.4 Analyze the filtrate by injecting 50 µL into the liquid chromatograph.

13.5 Identify the formaldehyde peak on the chromatogram using the retention time.

13.6 Measure the formaldehyde peak area by conventional methods.

13.7 Analyze the reagent blank (standard diluent) and the method blanks.

14. Calculation

14.1 Calculate the concentration of formaldehyde in the diluted emulsion polymer solution by reading from the calibration curve the ppm of formaldehyde corresponding to the calculated peak area.

14.2 Correct the formaldehyde concentration found in the diluted emulsion polymer solution for the dilution according to the following equation:

$$\text{Formaldehyde, ppm (test specimen)} = C \times D \quad (2)$$

where:

C = concentration of formaldehyde in the diluted emulsion polymer solution, ppm, and

D = dilution factor of the diluted emulsion polymer solution.

15. Report

15.1 Report the following information:

15.1.1 Report the average (arithmetic mean) of two determinations in ppm for formaldehyde and the difference between the two determinations as an estimation of the precision.

15.1.2 Report the results for the blank (13.6).

16. Precision and Bias [17]

16.1 *Precision*—The precision estimates are based on an interlaboratory study in which five different laboratories analyzed in duplicate on four days, four samples of emulsion polymers (see 1.1). The results obtained were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be:

Average HCHO (ppm)	Degrees of Freedom	Coefficient of Variation, %
900	15	4.40
300	15	7.07
10	15	13.34
1	15	25.77

and the between-laboratories coefficient of variation was found to be:

Average HCHO (ppm)	Degrees of Freedom	Coefficient of Variation, %
900	4	5.46
300	4	7.07
10	4	18.83
1	4	27.42

16.1.1 Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

16.2 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than as follows:

Average HCHO (ppm)	Degrees of Freedom	Coefficient of Variation, %	95 % Range
900	15	4.40	6.62
300	15	7.07	10.64
10	15	13.34	20.08
1	15	25.77	38.78

16.3 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than:

Average HCHO (ppm)	Degrees of Freedom	Coefficient of Variation, %	95 % Range
900	4	5.46	10.70
300	4	7.07	13.86
10	4	18.83	36.91
1	4	27.42	53.74

16.4 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring formaldehyde, bias cannot been determined.

[17] Supporting data are available from ASTM Headquarters. Request Research Report RR: D01-1085.

17. Keywords

17.1 emulsion polymers; free formaldehyde; liquid chromatography; post-column reaction