Designation: D5910 – 05 (Reapproved 2019)

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

This standard is issued under the fixed designation D5910; 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D2194 Test Method for Concentration of Formaldehyde Solutions

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E682 Practice for Liquid Chromatography Terms and Relationships

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.

[1] This test method is under the jurisdiction of ASTM Committee D01 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] 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.

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 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* [4] that can be heated to 95°C and contains a static mixing tee.[5,6]

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.

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.

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.[7]

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[8] 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.

SCHEMATIC OF LIQUID CHROMATOGRAPH AND POST-COLUMN REACTION SYSTEMS

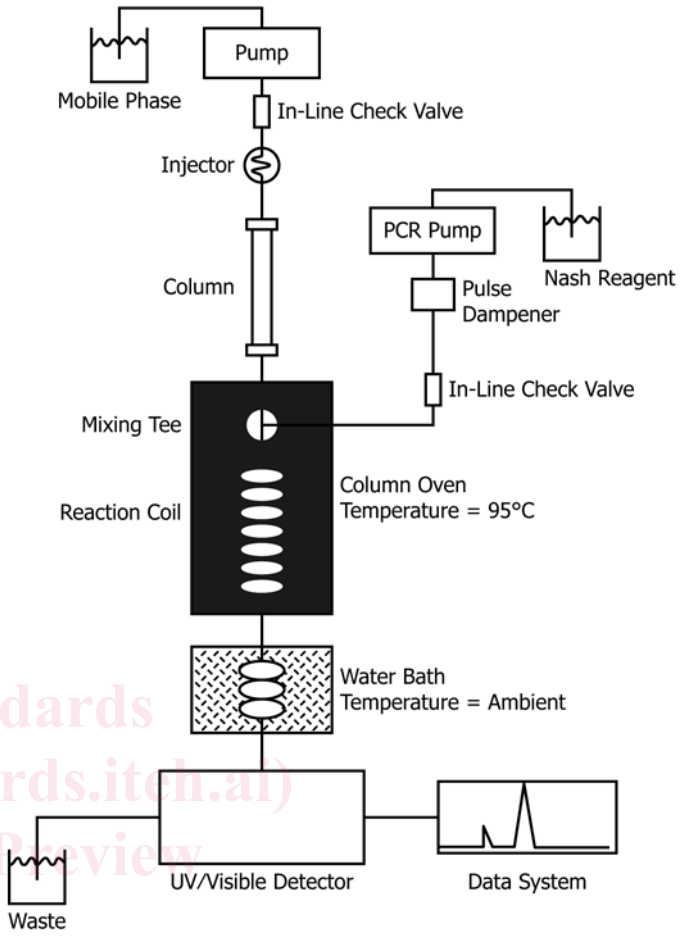

FIG. 1 Schematic of Liquid Chromatograph and Post-Column Reaction Systems

8. Configuration of Post-Column Reactor (PCR)

8.1 The post-column reagent passes through a pulse dampener[9] and an in-line check valve[8] 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.

[4] 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.

[5] 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.

[6] 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.

[7] 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.

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

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

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.[10] 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.

9.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water minimally conforming to Type II of Specification D1193, 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 % ($CH_3COCH_2COCH_3$).[11]

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[12] 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 E682. 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.

[10] *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.

[11] 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.

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