

T 600 om-11

TENTATIVE STANDARD – 1931

OFFICIAL STANDARD – 1933

REVISED – 1967

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CLASSICAL METHOD – 1983

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CAUTION:

This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Analysis of formaldehyde in aqueous solutions and of free formaldehyde in resins

1. Scope

1.1 This method is for the analysis of the formaldehyde content of aqueous solutions of the gas.

1.2 With the precautions given, it can also be used to determine the free (unreacted) formaldehyde content of resins used in paper treatment. Experience has indicated the method is adaptable to determination of free or unreacted formaldehyde in urea formaldehyde resins.

1.3 Most aldehydes and certain ketones will undergo the same reaction as formaldehyde. Thus the presence of other aldehydes will give erroneous results.

1.4 Acids and alkalis interfere in the titration, but this can be overcome by neutralization prior to reaction.

1.5 There are known instances where the formaldehyde is bound so loosely that it is very difficult not to hydrolyze the resin. Conducting the reaction at 0-5°C minimizes the hydrolysis.

2. Summary

A test specimen of the sample is reacted with an excess of sodium sulfite solution and the resulting sodium hydroxide is titrated with sulfuric acid using thymolphthalein indicator. The sulfite addition product is formed, liberating hydroxyl, which is titrated by the sulfuric acid: $\text{HCHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HCH}(\text{NaSO}_3)\text{OH} + \text{NaOH}$.

3. Significance

3.1 In past years, formaldehyde was used in the paper industry as a preservative in starch and glue solutions as well as clay coating colors. It was also used as a solubility modifier for glue, casein, and protein adhesives. It was also added to the solutions of coating color, or used as a part of an afterwash treatment.

3.2 Currently, the use of formaldehyde in the paper industry is quite low. This test method is maintained for adaptation and use in occasions when it is needed, particularly for detecting free or unreacted formaldehyde from urea formaldehyde resins in paper and related materials produced where formaldehyde may still be in use.

Approved by the Standard Specific Interest Group for this Test Method



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4. Apparatus

- 4.1 Analytical balance, 10 g capacity, capable of weighing to 0.001 g.
- 4.2 Pipet, 50 mL, or buret or graduated cylinder.
- 4.3 Glassware, 250 or 500 mL flasks or beakers.

5. Reagents

5.1 Sulfuric acid solution, 0.5N H₂SO₄, prepared according to TAPPI T 610 "Preparation of Indicators and Analytical Reagents and Standardization of Volumetric Solutions."

5.2 Sodium sulfite solution, 1.0M. This must be made fresh, and maintained cold (0-5°C). Dissolve 126 g of anhydrous sodium sulfite (Na₂SO₃) in water and dilute to 1000 mL.

NOTE 1: Sodium sulfite gradually oxidizes to sodium sulfate on exposure to air and, therefore, should be kept in a tightly closed container. For best results freshly prepared reagent should be used.

5.3 Thymolphthalein indicator solution, 0.1%. Dissolve 1.0 g of thymolphthalein in 100 mL of alcohol and dilute to 1000 mL with additional alcohol. Methyl, ethyl, or isopropyl alcohol is suitable.

6. Sampling and test specimens

- 6.1 If from a single vessel (jar, drum, tank), withdraw sufficient sample to perform the analysis in duplicate.
- 6.2 If from a lot of more than one vessel, obtain a sample according to a preselected plan or take aliquot parts from each vessel, combine, and withdraw the sample as in 6.1.
- 6.3 Weigh duplicate specimens of approximately 2 to 10 g to the nearest 0.001 g. Choose a specimen weight to allow the titration to be completed with from 20 to 50 mL of standard acid. Place in the 250-mL or 500-mL flask, bottle, or beaker. For example: If the expected value is 40 to 50% formaldehyde, weigh approximately 2 g; if 2%, weigh approximately 10 g.

7. Procedure

7.1 If the sample material contains any appreciable amounts of alkalinity or acidity, neutralize it to a thymolphthalein endpoint before proceeding to the actual formaldehyde determination.

NOTE 2: The specimen should be essentially neutral; 0.1% acidity (as formic acid) is equivalent to 0.065% formaldehyde. With commercial formaldehyde solutions it is normally not necessary to neutralize the sample before making the formaldehyde titration.

7.2 After weighing the specimen, as in 6.3, dilute with 25 mL distilled water and carefully add dilute sulfuric acid or sodium hydroxide to neutrality as determined by thymolphthalein.

7.3 If the specimen is a resin, add cracked ice made from distilled water to prevent any hydrolysis of the resin during titration.

7.4 Add 4-5 drops of indicator solution to the specimen in the flask, bottle, or beaker.

7.5 Add 50 mL of sodium sulfite solution to the flask. If a resin is being analyzed, the solution must be chilled to 0-5°C to prevent hydrolysis. Shake or stir gently to complete the solution.

NOTE 3: To avoid evaporation loss of formaldehyde, the entire specimen portion should be added to the sodium sulfite solution as quickly as possible and the solution swirled gently to insure mixing and to avoid loss of formaldehyde. Work rapidly. Keep sample container closed whenever possible. This strongly alkaline reaction mixture absorbs CO₂ from the air, leading to low results. The error is usually not significant if titration is completed within 10 min of sample preparation.

7.6 Immediately titrate to the colorless endpoint of the thymolphthalein indicator with the 0.5N sulfuric acid.

7.7 Wait a second or two to determine that all the liberated sulfite has reacted and add a few more drops of the dilute acid if necessary to complete the titration.

7.8 Make a blank determination by titrating the reagents used without the addition of a specimen.