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: \( \text{HCHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HCH(NaSO}_3\text{)}\text{OH} + \text{NaOH} \).

3. Significance

3.1 Formaldehyde finds many uses in the paper industry. A solution is added to starch and glue solutions and to clay coating colors as a preservative. In larger quantities, it is an insolubilizer for glue, casein and protein adhesives. It may be added to the solution or coating color or be used as part of an afterwash treatment.
3.2 Many formaldehyde-containing resins (amino-plasts) are also used as formaldehyde donors.

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.
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4.3 Glassware, 250 or 500 mL flasks or beakers.

5. Reagents

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

5.2 Sodium sulfite solution, 1.0 M. 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 duplication.

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 0.5 N 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.

8. Calculation

Calculate the percentage of formaldehyde as follows:

\[ \text{Formaldehyde, \%} = \frac{(M - B) \times (N) \times (0.03003) \times (100)}{W} \]
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where:

\[ M = \text{sulfuric acid titrant, mL} \]
\[ B = \text{sulfuric acid required in the blank determination, mL} \]
\[ N = \text{normality of sulfuric acid (0.5}\ N\text{ called for in test)} \]
\[ W = \text{weight of specimen, g} \]

(0.03003 is the milliequivalent weight of HCHO)

9. Report

Report the average percentage of formaldehyde calculated from the duplicate determinations.

10. Precision

10.1 Repeatability = 2\% of the reported percentage.
10.2 Reproducibility = 5\%.

10.3 Both values are according to the definitions in TAPPI T 1206 "Precision Statement for Test Methods" from a round robin on six widely different materials tested in duplicate in nine laboratories.

11. Additional information

11.1 Effective date of issue: May 10, 1983.
11.2 This method, formerly T 600 os-76, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superceded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.
11.3 Formaldehyde may be used in any of several forms. Formaldehyde readily polymerizes in aqueous solution. To prevent polymerization, methanol is added. A 37-40\% solution of formaldehyde in water, containing 15\% methanol, is known as formalin.
11.4 Paraformaldehyde is produced by evaporation of formaldehyde solution. Paraformaldehyde can be depolymerized in solution by either acid or base catalysts.
11.5 Formaldehyde is more stable in alcoholic solution.
11.6 Formaldehyde reacts with ammonia to form hexamethylene tetramine. This material is also used as a formaldehyde donor for many of the same applications. Formaldehyde is liberated by heating.
11.7 Related method: ASTM D 2194 (technically identical).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator.