WI 220802.09

T 493

BALLOT NO. 3 SARG

DRAFT NO. 2

DATE 6/1/2023

WORKING GROUP CHAIR N/A

SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

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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 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.

# Identification and determination of melamine resin in paper

*(Proposed REAFFIRMATION of Classical Method T 493 cm-10)*

## 1. Scope

1.1 This method, based on the 1954 work of Hirt, King, and Schmitt *(1)*, may be used for the detection and estimation of melamine resin in papers. It may be used in the presence of other additives, such as glue, glycerin, and rosin, but the presence of dyes or unbleached pulp may cause difficulties. The procedure was originally issued in 1963. A complete precision study of the procedure was never completed. The current (2010) use of melamine resin in paper is minimal, in part perhaps because of the use of formaldehyde to convert the melamine monomer to the

melamine resin. Based on limited current use of the method, users of the method should evaluate interferences and precision of the procedure in its intended application.

1.2 The procedure consists of a micro method intended for identification and semi-quantitative determination on small samples (1 to 4 mg) and a more precise macro method for samples one gram and heavier.

## 2. Summary

2.1 The procedure for both methods is carried out by refluxing the paper with 0.1*N* hydrochloric acid to extract the melamine resin, which is then hydrolyzed to melamine. The melamine is estimated by measuring its absorbance at 237 nm and at 260 nm.

## 3. Apparatus

3.1 *Spectrophotometer*, for making absorbance measurements in the ultraviolet range at 237 nm, and 260 nm to the nearest 0.01 absorbance unit.

3.2 *Absorption cells,* of quartz, for use with the spectrophotometer.

3.3 *Reflux assembly.*

3.3.1 For macro method, a 250-mL Erlenmeyer flask and water-cooled condenser, with standard tapered connections.

3.3.2 For micro method, a 5-mL Erlenmeyer flask and condenser, each with 14/2 standard taper joints. An air condenser, approximately 30 cm (12 in.) long may also be used for this method.

3.4 *Filter funnel,* with acid-washed, lint-free filter paper.

3.5 *Microfilter tube* (for micro method), coarse fritted glass, 10 mm (1/4 in.) diameter, approximately 3 mL capacity.

3.6 *Boiling chips,* porous porcelain or micro-porous carbon chips.

3.7 *Other apparatus* (for either method): a 5-mL pipet; 100- and 1000-mL volumetric flasks; 100-mL graduated cylinder. In addition, for the macro method, a 200-mL, and for the micro method, a 5-mL volumetric flask.

## 4. Reagents

4.1 *Hydrochloric acid,* 0.1*N* HCl, not standardized, and without significant absorbance at wavelengths of 237 and 260 nm with reference to distilled water.

4.2 *Melamine,* recrystallized as follows: Heat 200 mL of 5% NaOH solution to the boiling point, remove the source of heat, and add about 4 g of melamine. Stir until most of the material is dissolved (some always remains undissolved), filter hot and set aside for several hours to allow crystallization to occur. Filter with suction (using a Büchner funnel with hardened filter paper or medium porosity fritted glass), and wash with several portions of water at or below room temperature. Dissolve the crystals in 150 mL of boiling distilled water, filter if any turbidity is noted

and allow to crystallize overnight. Filter, wash with a few portions of distilled water and finally dry the melamine crystals on a watchglass for about 2 h at 105 ± 3°C (221 ± 5°F).

4.2.1 Determine the absorptivity of the melamine as follows:

4.2.1.1 Transfer about 120 mg, weighed to the nearest 0.1 mg, of the purified, dried melamine to a 1000-mL volumetric flask. Dissolve in 0.1*N* HCl, dilute to the mark with 0.1*N* HCl, and mix. Pipet 5 mL of this solution into a 100-mL volumetric flask, dilute to the mark with 0.1*N* HCl, and mix. This gives a solution containing about 0.6 mg of melamine per 100 mL. Measure the absorbance of this solution at 237 nm and at 260 nm using 0.1*N* HCl in the reference cell. A slit width of 0.8 nm is recommended.

4.2.1.2 Calculate the absorptivity of melamine at 237 nm by the formula:

$$a_{237} = \frac{A_{237}}{bc}$$

where:

$a_{237}$ = absorptivity at 237 nm
$A_{237}$ = absorbance at 237 nm
$b$ = cell light path, mm
$c$ = concentration of melamine, g/100 mL

4.2.1.3 Determine the absorptivity in duplicate; the values should lie between 79 and 81. If so, the indicated value may be used in the calculation for melamine content. The absorbance at 260 nm should not exceed 0.02 unit in a light path of 10 nm.

4.2.1.4 If the above criteria are not met, adjust the spectrophotometer or repurify the melamine.

## 5. Test specimen

5.1 *Macro method:* Allow the paper to come to moisture equilibrium with the atmosphere near the balance. From each test unit of a sample obtained in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product,” weigh a representative specimen of approximately 1.0 g to the nearest mg, and cut into pieces 0.5 cm to 1 cm square. If less than three test units are examined, weigh duplicate specimens from each unit. If the moisture content is not known, weigh specimens for moisture determination in accordance with TAPPI T 412 “Moisture in Paper and Paperboard.”

5.2 *Micro method:* Weigh a specimen of 1 to 4 mg to the nearest 0.01 mg. Cut into pieces 1 to 2 mm square. Estimate the moisture content if a separate specimen cannot be used for this purpose.

## 6. Procedure

6.1 *Extraction*

6.1.1 *Macro method.* Transfer the test specimen to the 250-mL Erlenmeyer flask. From a graduated cylinder, add 100 mL of 0.1*N* HCl (and a boiling chip), connect the condenser, and reflux for 1 h. Filter into a 200-mL volumetric flask using a lint-free filter paper, wash the specimen on the filter paper with about five portions of 0.1*N* HCl and dilute the filtrate to the mark with 0.1*N* HCl.

6.1.2 *Micro method:* Transfer the test specimen to a 5-mL Erlenmeyer flask. Add 2 or 3 mL of 0.1*N* HCl and a small boiling chip, attach the condenser and boil gently on a hot plate for 1 h. Pour through the fritted-glass filter tube into the 5-mL volumetric flask. Rinse the paper and extraction flask with 0.1*N* HCl, adding this to the extract. Cool the filtrate to room temperature, make up to exactly 5 mL and mix.

6.2 *Qualitative*

6.2.1 Fill a quartz absorption cell with the extract obtained according to the micro or macro method. Using 0.1*N* HCl as the reference solution, determine the absorbance at 220, 225, 228, 230, 235, 237, 240, and 260 nm.

6.2.2 The following absorbance characteristics are good evidence of the presence of melamine resin:

6.2.2.1 A maximum absorbance at 235 nm, falling off sharply at wavelengths longer than 237 nm.

6.2.2.2 An absorbance at 228 nm lower than that at 225 or 230 nm.

6.2.2.3 A sharp increase in absorbance at shorter wavelengths, exceeding the 235 nm peak at 220 nm.

6.2.3 A plot of the data (Fig. 1) is advantageous in illustrating the above characteristics but is usually not essential.

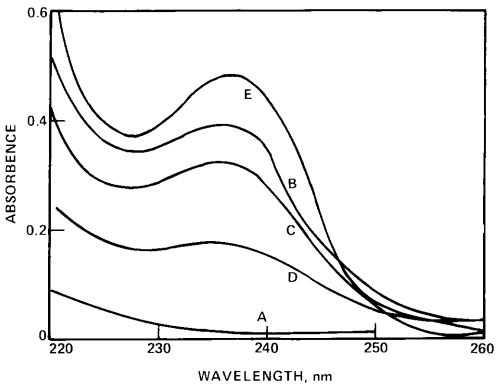



**Fig. 1.** Absorption spectra of melamine (Curve E) and of paper extracts (Curves A through D). A: glue-sized paper, 4 mg in 5 mL; B: glue-sized paper, 3% melamine resin, 1 mg in 5 mL; C: paper with 0.6% melamine resin, 4 mg in 5 mL; D: paper with 0.6% resin, 2 mg in 5 mL; E: pure melamine, 6 μg/mL.

**NOTE 1:** In the case of dyed or unbleached paper, enough coloring matter may be extracted to obscure some of these characteristics. A pre-extraction with 0.1*N* NaOH will often improve resolution with only a small loss of melamine. If this seems necessary, boil the test specimen with 0.1*N* NaOH solution, using a volume approximately equal to the HCl to be used for extraction. Decant the NaOH before adding the HCl.

6.3 *Quantitative*

6.3.1 Within 2 h of the hydrolysis step, measure the absorbance of the solution at 237 nm and at 260 nm using 0.1*N* HCl in the reference cell; temperature control is unnecessary. If the solution is too concentrated to allow an absorbance reading of less than about 0.6 at 237 nm, dilute an aliquot of the solution quantitatively with 0.1*N* HCl until the absorbance is within the range 0.2 to 0.5. These figures are arbitrary, but the accuracy of the measurement falls off at both the low and the high end of the scale.

**NOTE 2:** In the case of dyed or unbleached papers, enough coloring matter might be extracted to affect the absorbance of the solution.

**NOTE 3:** When using the micro method, the data obtained in the qualitative procedure may be used in the calculation.

## 7. Calculation

7.1 Calculate the percent melamine resin as follows:

$$\text{Melamine resin, \%} = 1.57 \times \frac{A_{237} - A_{260}}{a_{237}\, bW} fV$$

where

1.57 = 1.73 × 0.91; 1.73 being the factor to convert melamine to melamine resin and 0.91 an empirical factor to convert the result to the true value (*2*). (See Additional Information 10.3.2.)

$A$ = observed absorbance

$f$ = dilution factor (this is 1.0, if the refluxed solution is not diluted)

$V$ = volume of 0.1*N* HCl, mL (200)

$a_{237}$ = absorptivity of melamine at 237 nm

$W$ = moisture-free weight of the specimen, g

$b$ = cell light path, mm

7.2 When the paper contains glue, there is a slight interference and the quantity 0.01 × % glue is to be subtracted from the formula above. Usually, this interference is negligible. Except for very exacting work and with

paper containing small amounts of melamine, it may be ignored. If a correction seems necessary, determine the total nitrogen by TAPPI T 418 “Organic Nitrogen in Paper and Paperboard” and calculate the glue content after subtracting the nitrogen of the approximate melamine content. Both steps may be combined in the formula:

$$\text{Melamine resin, \%} = 1.605 \times \frac{A_{237} - A_{260}}{a_{237}\, bW}\, fV - 0.057 \times \text{\% total nitrogen}$$

**NOTE 4:** Although *melamine* is a definite chemical compound, *melamine resin* does not have a definite chemical structure, so that the factor of 1.73 is subject to some variation, depending on conditions during the manufacture of the resin.

## 8. Report

Report the average value of at least two determinations of melamine resin, to the nearest 0.01%, based on the moisture-free weight of the paper.

## 9. Precision

The standard deviation for a single specimen by one operator in one laboratory is 0.015% resin.

## 10. Keywords

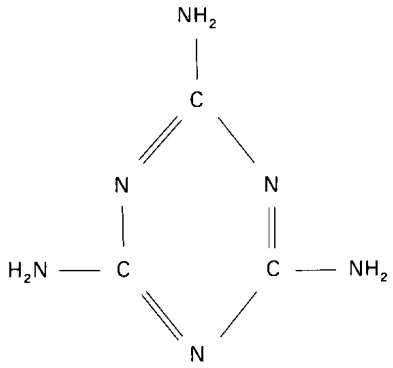
Paper, Polymelamines, Spectroscopy, Resin

## 11. Additional information

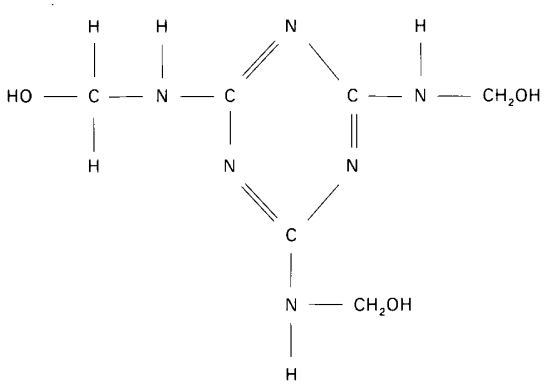
11.1 Effective date of issue: To Be Assigned.

11.2 In this revision, the reference to the related ASTM method is removed, that method having been withdrawn by ASTM. In addition, information has been added to the Scope calling attention to the limited available use and knowledge of this procedure.

11.3 The structure for melamine is:



11.3.1 In melamine resin, the amine groups have been reacted with formaldehyde to form the trimethylol derivative:



11.3.2 The factor for converting melamine values to melamine resin values may be obtained in two ways:

11.3.2.1 The factor may be calculated from the nitrogen contents of melamine and of melamine resin. Calculated from the formula of melamine, $C_3N_3(NH_2)_3$, the percentage of nitrogen is 66.7. The percentage of nitrogen in melamine resin is about 38.5 (manufacturer's data); therefore, 66.7/38.5 = 1.73.

11.3.2.2 Melamine resin may be hydrolyzed to melamine and the melamine determined by the spectrophotometric method. A weighed quantity of melamine resin is refluxed for one hour in 0.1*N* HCl and the melamine determined as usual. The weight of melamine resin taken divided by the weight of melamine found gives the desired conversion factor. These two methods should give concordant results.

11.4 High values may be caused by interfering substances such as conjugated fatty acids. High values may also be obtained in the analysis of melamine resins by the spectrophotometric method. This is attributed to incomplete hydrolysis of the resin, as the resin has a higher absorption at 237 nm than melamine (*2*).

11.5 A list of additional references will be found in *Tappi* **50** (7): 175A (1967).

## Literature cited

1. Hirt, R. C., King, F. T., and Schmitt, R. G., *Anal. Chem.* **26**: 1273 (1954).
2. Morath, J. C., and Woods, J. T., *Anal. Chem.* **30**: 1437 (1958).

*Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department.* ■