

**NOTICE: This document is a TAPPI Standard in ballot. Although available for public viewing, it is still under TAPPI's copyright and may not be reproduced or distributed without permission of TAPPI. This document is current under review to be maintained as a TAPPI Standard.**

WI \_\_\_\_\_ 230809.02 \_\_\_\_\_

T \_\_\_\_\_ 282 \_\_\_\_\_

BALLOT NO. \_\_\_\_\_ 02 SARG \_\_\_\_\_

DRAFT NO. \_\_\_\_\_ 1 \_\_\_\_\_

DATE \_\_\_\_\_ October 26, 2023 \_\_\_\_\_

WORKING GROUP  
CHAIR \_\_\_\_\_ N/A \_\_\_\_\_

SUBJECT  
CATEGORY \_\_\_\_\_ Pulp Properties \_\_\_\_\_

RELATED  
METHODS \_\_\_\_\_ See "Additional Information" \_\_\_\_\_

**CAUTION:**

This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. 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 method, the user must 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.

## **Hexeneuronic acid content of chemical pulp**

### *Five-year review of Official Method T 282 om-2019*

#### **1. Scope**

This method describes a procedure to determine hexeneuronic acid groups (HexA) in chemical pulps. HexA affects the kappa number determination by reaction with permanganate, and can react with certain bleaching chemicals, e.g. chlorine dioxide and ozone, but not with some others such as oxygen and peroxide.

## 2. Summary

The method is based on the highly selective hydrolysis of HexA from a pulp sample in a mercuric chloride-sodium acetate solution. Complete hydrolysis of HexA from pulps is achieved within 30 minutes by choosing the appropriate hydrolysis conditions (the concentration of the hydrolysis agent and the composition of the hydrolysis solution) and temperature. The amount of HexA is directly determined by UV spectrophotometry from the resulting hydrolysis solution (1). A dual-wavelength spectroscopic technique (at 260 and 290 nm) is used to eliminate the spectral interference from the leached lignin in the resulting solution.

## 3. Significance

The presence of the HexA increases chlorine dioxide consumption in chlorine dioxide bleaching. It also causes overestimation of the residual lignin in pulps, which could lead to over dosage of peroxide in peroxide bleaching. Even a small amount of HexA can bond with transition metals and reduce pulp brightness stability. These effects are more significant for hardwood chemical pulps. Because pulping temperature and alkaline profiles can affect HexA formation and degradation, the variation of HexA in chemical pulps is significant. Accurate quantification of HexA content in chemical pulps has practical importance.

## 4. Definition

The main uronic acid group in chemical pulps is 4-deoxy- $\beta$ -L-threo-hex-4-enopyranosyluronic acid (hexeneuronic acid, HexA). This acid does not exist in native wood but is formed in chemical (alkaline) pulping through  $\beta$ -elimination of methoxyl groups from 4-methylglucuronic acid (MeGlcA).

## 5. Apparatus

5.1 A UV-spectrophotometer with a diode array detector or spectrum scanning capability for measuring absorption at multiple wavelengths.

5.2 *Sample cell*, optical pass of about 10 mm, such as a quartz or fused silica cell.

5.3 *Sample vial*, 20 mL, can be sealed by a septum.

5.4 *Water bath*.

5.5 *Plastic syringe*, 3 mL.

5.6 *Syringe filter*, 0.2  $\mu$ m.

## 6. Reagents

6.1 *Mercuric chloride* ( $\text{HgCl}_2$ , analytical grade).

6.2 *Sodium acetate trihydrate* ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , analytical grade).

6.3 *Distilled water*.

6.4 Weigh  $6 \pm 0.006$  g of  $\text{HgCl}_2$  and  $7 \pm 0.007$  g of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and add them into a beaker together with about 500 mL distilled water for dissolution. Transfer the solution to a 1-L volumetric flask and fill distilled water to the 1-L mark. This makes a hydrolysis solution of 0.6% mercuric chloride and 0.7% sodium acetate.

## 7. Pulp sample

Obtain an unbleached pulp sample, equivalent to 5 g air-dried pulp handsheet. Wash the pulp thoroughly using distilled water for slush pulps. Determine the moisture content and the oven-dry weight ( $w$ ) of the pulp sample using TAPPI T 210 (“Sampling and Testing Wood Pulp Shipments for Moisture”).

## 8. Procedure

8.1 Weigh  $0.05 \pm 0.0005$  g pulp sample using an analytical balance accurate to  $\pm 0.0002$  g with known moisture content from the sample obtained from Section 7 and add it into a 20-mL vial containing 10 mL of hydrolysis solution. Seal the vial by a septum. Handshake the vial to mix the chemicals with the sample. For samples where anticipated level (or the measured level of HexA found in a preliminary analysis) is below  $5 \mu\text{mol/g}$ , the analysis should be repeated using a  $0.5 \pm 0.005$  g sample to increase sensitivity.

8.2 Heat the vial for  $30 \pm 0.5$  minutes in a water bath at  $65 \pm 1^\circ\text{C}$ .

8.3 Remove from water bath and cool with tap water to room temperature.

8.4 Use a 3-mL plastic syringe to retrieve the resulting solution from vial.

8.5 Use a 0.2- $\mu\text{m}$  syringe filter on the plastic syringe to filter finers and fines before dispensing the filtrate into a silica sampling cell for UV absorption measurements.

8.6 Conduct UV absorption measurements of the filtered solution in the 10-mm path length quartz or fused silica sample cell. Record the absorption signals at 260 and 290 nm. Sample dilution may be necessary for UV measurements to ensure absorption signal at 260 nm is not saturated.

8.7 Conduct UV absorption measurements of the fresh hydrolysis solution (as the blank) in a 10-mm path length sample cell.

## 9. Calculation

9.1 *Absorption signal determination*: Spectrophotometers automatically subtract the measured absorbance of the blank (fresh hydrolysis) solution from the absorbance of the filtered sample solution. Calculate HexA content according to 9.2 using the absorption signal readings from the instrument directly.

9.2 HexA content determination:

$$C_{HexA} (\mu mol / g) = 0.287 \times \frac{(A_{260} - 1.2A_{290}) \cdot V(mL)}{w(g)}$$

where

- 0.287 = calibration constant obtained using a standard pulp (2). This calibration constant can be universally used to calculate HexA content in any pulps. There is no need to conduct calibration.
- 1.2 = ratio between lignin absorption at 260 nm and 290 nm that is used to correct lignin absorption on HexA determination (1).
- $V$  = the volume of the testing hydrolysis solution in mL.
- $w$  = weight of the oven-dry mass of the pulp sample used in hydrolysis in grams.

## 10. Report

Report HexA content as an average of two determinations in  $\mu mol/g$  to three significant figures.

## 11. Precision

11.1 A round robin study was conducted by 5 laboratories: two from the United States, one from Canada, one from China, and one from Spain. Three kraft eucalyptus pulp samples were produced and sent to these 5 laboratories. The variations in HexA among these samples were not significant but apparent. The reported data were averages of replicate measurements in each laboratory. The repeatability and reproducibility were determined in accordance with the definitions of the terms in TAPPI T 1200 “Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility.”

11.2 Repeatability: (within a laboratory) = 3%.

11.3 Reproducibility: (between laboratories) = 9%.

## 12. Safety

Collect the hydrolysis solution that may contain mercuric compounds for proper disposal.

## 13. Keywords

Hexeneuronic acid, Acid groups, Chemical pulps, Ultraviolet spectroscopy, Hydrolysis

## 14. Additional information

13.1 Effective date of issue: To be assigned.

13.2 The 2013 revision added precision data so that this standard could be upgraded to Official Method status. Several editorial changes were also made.

## Literature cited

1. Chai, X.S., Zhu, J.Y., and Li, J., "A Simple and Rapid Method to Determine Hexenuronic Acid Groups in Chemical Pulps," *J. Pulp Paper Sci.*, **27**(5):165 (2001).
2. Gellerstedt, G. and Li, J., "An HPLC method for the quantitative determination of hexenuronic acid groups in chemical pulp", *Carbohydr. Res.*, **294**:41, 1996.
3. Zhu, J.Y., Zhou, H.F., Chai, X.S., Johannes, D., Pope, R., Valls, C., Roncero, M.B., "Inter- Laboratory Comparisons of HexA Measurements in Kraft Eucalyptus Pulps using a UV-Vis Spectroscopic Method" *TAPPI J.* **13**(1):57, 2014.

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

