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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 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 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

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 groups in chemical pulps is 4-deoxy- β -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 β -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 *A water bath*.
- 5.5 *Plastic syringe*, 3-mL.
- 5.6 *Syringe filter*, 0.2 μm .

6. Reagents

- 6.1 *Mercuric chloride* (HgCl, analytical grade)
- 6.2 *Sodium acetate trihydrate* (CH₃COONa • 3H₂O, analytical grade)
- 6.3 *Distilled water*
- 6.4 Weigh 6 g of HgCl and 7 g of CH₃COONa • 3H₂O 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. Washing the pulp may be necessary for slush or other pulps. Determine the moisture content and the oven-dry weight (*w*) of the pulp sample using TAPPI T 210 (“Weighing, Sampling and Testing Pulp for Moisture”).

8. Procedure

- 8.1 Accurately weigh 0.05 g pulp sample 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.
- 8.2 Heat the vial for about 30 minutes in a water bath at 60-70°C.
- 8.3 Remove from water bath and cool with tap water to a room temperature.
- 8.4 Use a 3-mL plastic syringe to retrieve the resulting solution from vial .
- 8.5 Use a 0.2- μm 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.
- 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:

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

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 $\mu\text{mol/g}$ to three significant figures.

11. Precision

11.1 Repeatability:

Sample No.	Pulp weight, g**	HexA, $\mu\text{mol/g}$ pulp
1	0.0498	43.8
2	0.0526	45.6
3	0.0472	44.1
4	0.0490	45.3
5	0.0523	45.5
Mean		44.9
RSTD		1.9%

11.2 *Reproducibility and comparability.* The comparison and reproducibility of the above proposed method were demonstrated by 5 pulp samples measured by the Institute of Paper Science and Technology, Atlanta, Georgia, USA and the Forestry and Forest Products Research Center, Natural Resources and the Environment (NRE); CSIR, South Africa (3). As shown in Figure 1, the measurements correlate very well with a systematic difference of about 12%, which most likely could be due to differences in pulp moisture content measurements. The method was also compared with the KTH (Royal Institute of Technology, Sweden) method (3). The KTH method (2) shows low HexA contents. But the results from the two methods correlate very well. The low results from the KTH method may due incomplete hydrolysis.

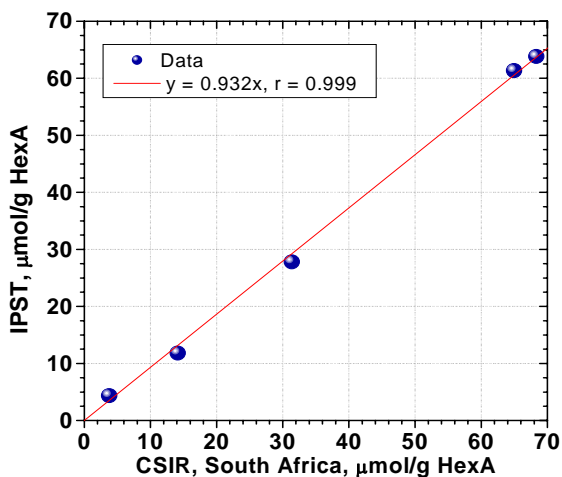


Fig. 1. Reproducibility and comparability data

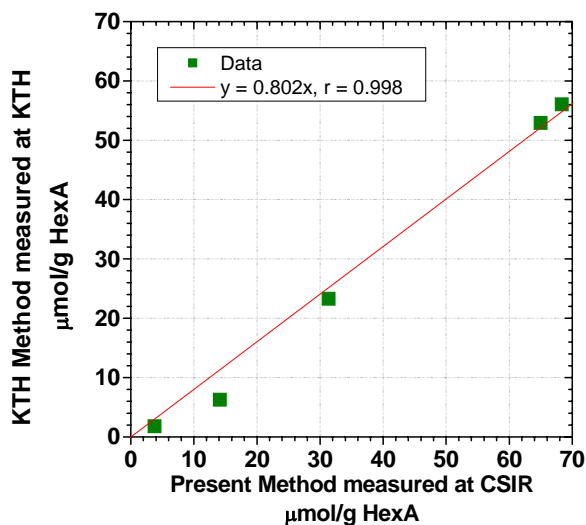


Fig. 2. Comparison of the proposed method with the KTH method (2).

12. Safety

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

13. Additional information

Effective date of issue: October 30, 2007.

14. Keywords

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

Literature cited

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

Zhu, J. Y. and X. S. Chai. Hexeneuronic acid content of chemical pulp. TAPPI Test Method T282 pm-07. Atlanta, GA : TAPPI, c2007. 4 p.