Carboxyl content of pulp
(Ballot for reconfirmation T 237 cm-08 as a Classical Method)
(No changes from Draft 1; second ballot required due to low percentage of votes returned on Ballot 1)

1. Scope

This method describes a procedure for the determination of the content of carboxyl groups in bleached and delignified pulps. Lignin and lignin degradation products, especially sulfonic acid groups in sulfite pulps (1) interfere with the determination of carboxyl content, and the method is not applicable to unbleached and semi-bleached pulps.

2. Summary

Pulp is extracted (de-ashed) with dilute hydrochloric acid, washed, reacted with sodium bicarbonate-sodium chloride solution, and filtered. The filtrate is titrated with 0.01N hydrochloric acid to methyl red end point (2).
3. **Significance**

Carboxyl groups represent the ion-exchange capacity of a pulp, i.e., the ability to absorb metallic cations during the processing. In paper pulps the carboxyl groups contribute to the bonding of fibers and formation of paper and to the retention of rosin size. On the other hand, the absorbed cations are largely responsible for discoloration of pulp and paper on drying. Stability and electric properties of condenser paper depend mainly on the amount of metal ions bound by the carboxyl groups. In dissolving pulps carboxyl groups increase viscosity and decrease pulp solubility.

4. **Definition**

The carboxyl groups, -COOH, are acidic groups attached to cellulose chains and are formed mainly by oxidation of cellulose during pulping and bleaching processes. A certain level of carboxyl groups is also associated with hemicellulose.

5. **Apparatus**

5.1 *Disintegrator*, such as a Waring or an equivalent blender or mixer, suitable for wet disintegration of pulp.

5.2 *Filtering funnels*, 150-mL and 300-mL, with fritted glass discs of coarse porosity (nominal pore size 40 to 50 μm).

5.3 *Filtering flasks*, 250-mL and 500-mL.

5.4 *Other equipment*: Erlenmeyer flask (tared), 250-mL, with glass stopper; pipets, 25- and 50-mL; buret, 50-mL; graduated cylinder, 250-mL; beaker, 600-mL; glass stirring rods.

6. **Reagents**

6.1 *Hydrochloric acid*, 0.1N HCl, not standardized. Add 8.45 mL concentrated HCl to approximately 900 mL distilled water. Make to a total volume of 1000mL.

6.2 *Hydrochloric acid*, 0.010N HCl, standardized to the nearest 0.0002N. (See TAPPI T 610 “Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions” for preparation and standardization of HCl.)

6.3 *Sodium hydroxide solution*, 0.01N NaOH, not standardized. Dissolve 0.40 g of solid NaOH in 1000 mL of water.

6.4 *Sodium bicarbonate-sodium chloride solution*. Dissolve 0.84 g of NaHCO₃ and 5.85 g of NaCl in water and dilute to 1000 mL.

6.5 *Methyl red indicator*, 0.1% solution, in ethanol.

6.6 *Distilled water*, saturated with carbon dioxide (CO₂) gas.
7. **Sample**

Obtain a sample of bleached pulp, equivalent to about 10 g oven-dry, in accordance with TAPPI T 210 “Weighing, Sampling and Testing Pulp for Moisture.” If the sample is a pulp sheet, tear or cut it into pieces about 10 mm across.

8. **Test specimens**

8.1 Allow the sample to come to moisture equilibrium in the atmosphere near the balance and weigh out two test specimens of 2.5 ± 0.1 g to the nearest 1 mg.

8.2 At the same time weigh out a specimen for moisture determination in accordance with TAPPI T 210 “Sampling and Testing Wood Pulp Shipments for Moisture.”

9. **Procedure**

9.1 Disintegrate the test specimen in distilled water and filter on a 300-mL filtering funnel. Place the pulp pad in a 600-mL beaker, add 250 mL of 0.1N HCl and stir with a glass rod to disperse. Allow the dispersion to stand at room temperature for 120 min.

9.2 Filter the pulp on a 150-mL filtering funnel and wash with distilled water saturated with CO₂. Continue washing until the last 10 to 20 mL of the filtrate, after boiling for 1 min, does not require more than 1 or 2 drops of 0.01N NaOH to give a yellow color with methyl red indicator.

9.3 Transfer the pulp quantitatively to a tared 250-mL Erlenmeyer flask and weigh to the nearest 0.1 g. Add 50.0 mL of sodium bicarbonate-sodium chloride solution, stopper the flask, and shake to obtain a homogeneous slurry. Allow to stand at room temperature for 60 min.

9.4 Filter the slurry on a dry 150-mL funnel into a clean and dry flask. Pipet 25.0 mL of the filtrate into an Erlenmeyer flask and titrate with 0.010N HC1 using methyl red indicator. When the first change in color occurs, boil the solution for 1 min to expel the carbon dioxide and continue the titration to the pink end point. Record volume of 0.010N HC1 consumed as “A.”

9.5 Pipet 25.0 mL of the sodium bicarbonate-sodium chloride solution into an Erlenmeyer flask and titrate with 0.010N HC1 as in 9.4. Record volume of 0.010N HC1 consumed as “B.”

10. **Calculation**

Calculate the carboxyl content in milliequivalents (meq) per 100 g of oven-dry pulp:

\[
\text{Carboxyl, meq/100 g} = \left( B - \left[ A + \left( A \times \frac{C}{50}\right) \right] \right) \times N \times \left( \frac{200}{W} \right)
\]
where
\[ A = \text{volume in mL of } 0.010N \text{ HCl consumed in titration of } 25 \text{ mL of the pulp filtrate.} \]
\[ B = \text{volume in mL of } 0.010N \text{ HCl consumed in titration of } 25 \text{ mL of the sodium bicarbonate-sodium chloride solution, mL} \]
\[ C = \text{weight of water in the pulp pad, i.e., weight of wet pad (9.3) minus oven dry weight of test specimen (8.1), g (Note: The unit for this calculation is actually “mL” as 1 g water = 1 mL.)} \]
\[ N = \text{normality of HCl used in titration} \]
\[ W = \text{weight of oven-dry test specimen, g} \]
\[ 50 = \text{volume of sodium bicarbonate-sodium chloride solution added to the test specimen, mL} \]
\[ 200 = \text{derived as } 2 \times 100, \text{ where } 2 \text{ is a factor to account for } 25 \text{ mL aliquot taken for titration, and } 100 \text{ is to express the result on } 100 \text{ g of pulp} \]

11. **Report**

Report carboxyl content as an average of two determinations to two significant figures.

12. **Precision**

12.1 **Repeatability:**

<table>
<thead>
<tr>
<th>Carboxyl content, meq/100 g</th>
<th>Repeatability, meq/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20 to 5.0</td>
<td>0.13</td>
</tr>
<tr>
<td>5.1 to 10</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The data were obtained within a single laboratory and are expressed in accordance with TAPPI T 1206 “Precision Statement for Test Methods.”

12.2 **Reproducibility and comparability:** not known.

13. **Keywords**

Pulp, Carboxyl groups, Bleached pulps, Cellulose, Ion exchange

14. **Additional information**

14.1 **Effective date of issue:** To be assigned.

14.2 An alternative methylene blue method contained in an earlier version of T 237 was previously deleted as being intricate and time-consuming. It may be useful, however, for application on small samples and on materials with very low carboxyl content. The method is described in the literature (3).
14.3 Comparative data on carboxyl determination by various methods are published (3).
14.4 Related method: ASTM D 1926.
14.5 This method was reclassified as a Classical Method by committee action in 1998.

References


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