

## *Pulp*

# Total acidic group content

## *Conductometric titration method*

### **0 Introduction**

The charge of cellulosic fibres is due to the dissociation of acidic groups. In most pulp grades, weak carboxylic acid groups are the only type of acidic group present. However, sulphonic acid groups are present in some pulp grades like, for instance, CTMP and sulphite pulps.

All the main components of cellulosic fibres, i.e. cellulose, hemicellulose, lignin and extractives, contain charged groups. In most pulp grades, uronic acid side-groups in xylan are the most frequent acidic groups present. In the wet end of the papermaking process, these charged groups strongly affect the interactions between pulp fibres and between fibres and added chemicals. The ionic groups are also important for the metal binding and swelling of the fibres, as well as the strength and the optical properties of the paper. Hence, the charge properties of cellulosic materials are important in many applications.

Charge properties of cellulosic materials have been determined by several methods. Among the most common methods are conductometric titration (12.1), potentiometric titration (12.1, 12.2), the Mg-elution method (12.3), polyelectrolyte adsorption (12.4), and zeta potential measurements (12.5). It has been reported that the total amount of acidic groups obtained by potentiometric or conductometric titration agrees well with results obtained with other methods (12.1, 12.6). Sulphonic acid groups can be determined by the Quinoline method (12.7), and it has been reported that sulphonic and carboxylic acid

groups can be determined separately by conductometric titration (12.1). However, a comparison between the Quinoline method and conductometric titration for a CTMP pulp indicated that the conductometric titration method overestimates the amount of sulphonic acid groups. Hence, this SCAN-test method based on conductometric titration includes only the determination of the total amount of charged groups, and not the amounts of carboxylic and sulphonic acid groups separately. Other acidic groups like phenolic hydroxyl groups are not measured by conductometric titration, but such groups probably do not influence the determination significantly (12.8).

### **1 Scope**

This SCAN-test method describes a procedure for the determination of the total acidic group content (the sum of carboxylic and sulphonic acid groups) in pulp.

### **2 References**

- |             |   |
|-------------|---|
| EN 20638    | Pulps – Determination of dry matter content (ISO 638) |
| EN ISO 5263 | Pulps – Laboratory wet disintegration                 |

*Note* – SCAN-test has withdrawn a number of test methods from January 2002 and refers instead to the corresponding EN and/or ISO Standards.

### 3 Definitions

For the purpose of this Method, the following definitions apply:

3.1 *Strong acidic groups* – Sulphonic acid groups,  $-\text{SO}_3\text{H}$ , which ionise even under strongly acidic conditions ( $\text{pK}_a \sim 1$ ).

*Note 1* – In CTMP and sulphite pulps, sulphonic acid groups are introduced in the lignin structure.

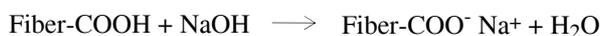
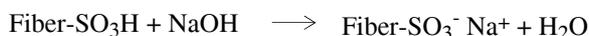
3.2 *Weak acidic groups* – Carboxylic acid groups,  $-\text{COOH}$ , which dissociate under weakly acidic conditions ( $\text{pK}_a = 3-5$ ).

*Note 2* – All pulp grades contain carboxylic acid groups.

3.3 *Total amount of acidic groups* – The sum of sulphonic and carboxylic acid groups.

### 4 Principle

The fibres are converted to the proton-form, i.e. all acid groups receive  $\text{H}^+$  as counter-ions, and are then titrated with sodium hydroxide. The sulphonic acid groups and the carboxylic acid groups react with the added sodium hydroxide:



Prior to titration, some salt (sodium chloride) is added to the titration vessel in order to improve the accuracy of the determination (12.8). Due to ion exchange, the higher sodium ion concentration causes some liberation of protons.

The titration is characterised by three distinct phases as illustrated by the appearance of the titration curve, *Figure 1*. The total amount of acidic groups can be determined from the 2nd intersection point, as illustrated in the *figure*.

### 5 Reagents

All reagents shall be of analytical grade.

5.1 *Sodium chloride solution*,  $c(\text{NaCl}) = 0,05 \text{ mol/l}$ .

5.2 *Hydrochloric acid*,  $c(\text{HCl}) = 0,010 \text{ mol/l}$ .

5.3 *Hydrochloric acid*,  $c(\text{HCl}) = 0,1 \text{ mol/l}$ .

5.4 *Sodium hydroxide solution*,  $c(\text{NaOH}) = 0,05 \text{ mol/l}$ . The concentration accuracy should be  $0,001 \text{ mol/l}$ . Check the concentration by using the procedure described in 8.2.

5.5 *Distilled or deionised water*

### 6 Apparatus

6.1 *Balance*, with a resolution of 1 mg.

6.2 *Vacuum filter assembly*, consisting of a Büchner funnel (11 cm diameter) and a vacuum flask.

6.3 *pH meter*

6.4 *Conductivity meter*

6.5 *Precision burette*

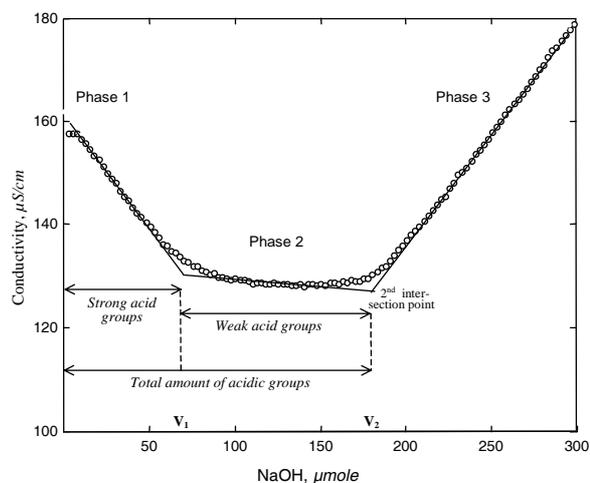
6.6 *Magnetic stirrer*, with a magnet.

6.7 *Titration vessel*, volume 600 ml.

6.8 *Oven*, which can be maintained at  $(105 \pm 1) \text{ }^\circ\text{C}$ .

6.9 *Glass fibre filters*

6.10 *Nylon sieve*, with a hole diameter of  $76 \text{ } \mu\text{m}$  (200 mesh).



*Figure 1. Determination of the total amount of charged groups in a CTMP by conductometric titration.*

*Phase 1:* The conductivity of the solution decreases when the strong acidic groups are neutralised with NaOH. When no strong acidic groups are present, a slight reduction in conductivity will initially appear due to neutralisation of the protons liberated by the salt.

*Phase 2:* Neutralisation of carboxylic groups during which the conductivity remains essentially unchanged. The added sodium ions ( $\text{Na}^+$ ) are adsorbed as counter-ions to the carboxylic acid groups, and the dissociated protons are neutralised by the added hydroxide ions ( $\text{OH}^-$ ).

*Phase 3:* Accumulation of NaOH in excess leads to an increase in conductivity.

## 7 Sample preparation

### 7.1 Storage and prewashing

If the sample is in a dry form, it shall, prior to washing, be soaked and disintegrated in accordance with EN ISO 5263.

Dilute between 3 g and 5 g (oven dry weight) pulp to 1 % concentration using distilled water (5.5). Filter it on a Büchner funnel (6.2) using a nylon sieve (6.10). If the filtrate is cloudy, recycle it in order to keep the fines. The water-washed pulp sample (of approx. 20 % dry matter content) may be stored in a refrigerator for later analysis or protonized directly according to the procedure described in 7.2.

*Note* – Is it not recommended to store wet pulp samples longer than 1 month in a refrigerator, due to the microbiological growth sensitivity of wet samples. Drying or freezing of pulp samples may cause a small reduction in the measured amount of charged groups.

### 7.2 Protonization

Suspend the prewashed pulp sample in hydrochloric acid (5.3) at 1 % concentration. Let it stand for 15 minutes. Filtrate the suspension on a Büchner funnel (6.2), remove excess acid by washing repeatedly with deionised water (5.5) and recycle the filtrate until the conductivity of the washed filtrate is less than 5 µS/cm.

## 8 Titration procedure

### 8.1 Conditions

Perform the titration at room temperature. The temperature variation during the titration may not exceed  $\pm 1$  °C. Stir the pulp sample using a magnetic stirrer (6.6).

### 8.2 Checking the sodium hydroxide solution

Add 485 ml of distilled water (5.5), 10 ml of sodium chloride solution (5.1) and 5 ml of hydrochloric acid (5.2) to a titration vessel (6.7). Titrate with sodium hydroxide solution (5.4), and determine the exact concentration of the sodium hydroxide solution,  $C_1$ , from the V-shaped graph.

### 8.3 Titration of a pulp sample

Run the titration in duplicate.

Add approx. 1 g oven-dry pulp to the titration vessel (6.7). Add 490 ml of distilled water (5.5) and 10 ml of sodium chloride solution (5.1) in order to obtain a 1 mM NaCl solution concentration during titration. A total sample volume of 500 ml is recommended.

Titrate the pulp suspension, by adding sodium hydroxide solution (5.4) from a precision burette (6.5). Addition steps of about 0,1 ml sodium hydroxide

solution are recommended, and the time between the additions should be from 10 s to 30 s. Record the conductivity after each addition. The titration is completed when extrapolation of the alkaline part (phase 3) of the titration curve can be properly done, typically at about pH 10,5. From the titration curve, read off the volume,  $V_2$ , of sodium hydroxide solution consumed at the 2nd intersection point.

Filter the pulp suspension using a Büchner funnel (6.2) onto a pre-weighed glass fibre filter (6.9). Flush the vessel with a small amount, approx. 100 ml, of distilled water (5.5). Dry the filtered pulp sample according to EN 20638.

After drying, cool the pulp sample with the attached glass fibre filter in a desiccator and weigh it.

## 9 Calculation

Calculate the oven-dry weight of the sample,  $m$ . The calculation of the total amount of acidic groups from the titration curve is illustrated for a CTMP in *Figure 1*.

To obtain the total amount of acidic groups, extrapolate and locate the point of intersection of the second and the third linear portions of the curve at the 2nd intersection point.

Calculate the total acidic group content from the equation:

$$X = \frac{C_t \cdot V_2}{m} \quad [1]$$

where

$X$  is the total acidic group content, in µmol/g;

$C_t$  is the concentration of the sodium hydroxide solution, in µmol/l;

$V_2$  is the volume of the sodium hydroxide solution consumed at the 2nd intersection point, in litres;

$m$  is the oven-dry weight of sample, in gram.

Calculate the mean. Report the total acidic group content to the nearest integer.

## 10 Report

The test report shall include reference to this SCAN-test Method and the following particulars:

- date and place of testing;
- a precise identification of the sample;
- the result;
- the dry weight of the pulp sample;
- any departure from the standard procedure and any other circumstances that may have affected the results.

**11 Precision**

**11.1 Repeatability**

Four laboratories tested three chemical pulps (containing only carboxylic acid groups) and a bleached CTMP (containing both carboxylic acid groups and sulphonic acid groups). Each pulp was tested five times in each laboratory. The average coefficient of variation (CV) between replicates was 3,3 %. The results for the pulps separately were as follows:

Pulp	Total acidic group content, $\mu\text{mol/g}$	CV, within labs, %
Bleached TMP	160	2
Unbleached softwood kraft	110	3
ECF bleached softwood kraft pulp	40	5
Bleached CTMP	155	3

**11.2 Reproducibility**

The average coefficient of variation (CV) between laboratories was 5,8 %. The results for the pulps separately were as follows:

Pulp	Total acidic group content $\mu\text{mol/g}$	CV between labs, %
Bleached TMP	160	2
Unbleached softwood kraft pulp	110	3
ECF bleached softwood kraft pulp	40	10
Bleached CTMP	155	4

**12 Literature**

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