

White and green liquors

Total, active and effective alkali

Potentiometric titration

0 Introduction

This SCAN-test Method has been developed for use in laboratories employing electrometric titration for the analysis of white and green liquors. The results obtained by the method described in this Method do not differ significantly from those obtained by the method described in SCAN-N 2 (the traditional titration using barium chloride precipitation, the formaldehyde reaction and visual end point detection).

1 Scope and field of application

This SCAN-test Method specifies an electrometric titration procedure for the determination of total, active and effective alkali in normal white and green liquors obtained and used in the kraft or sulphate pulping process. This Method may not be used for the analysis of liquors such as oxidized white liquors which contain significant amounts of polysulphides. The definitions given below do not apply to such liquors. This Method is not intended for the determination of particular ionic species, such as sulphides or carbonates.

2 Definitions

2.1 *Total alkali (of white and green liquors):*

The total concentration of alkaline constituents determined by titration of a sample of the liquor with strong acid to the third inflexion point according to the procedure specified in this Method.

Note -See also the Annex.

2.2 *Active alkali (of white and green liquors):*

The total concentration of alkaline constituents, except carbonates, as determined by titration of a sample of the liquor with strong acid according to the procedure specified in this Method.

Note - In practice, active alkali is considered to be the sum of the concentrations of hydroxyl and hydrosulphide ions, including hydroxyl ions formed by hydrolysis of sulphides. See also the Annex.

2.3 *Effective alkali (of white and green liquors):*

The concentration of strongly alkaline constituents determined by titration of a sample of the liquor with strong acid to the first inflexion point according to the procedure specified in this Method.

Note - In practice this is considered to be the concentration of hydroxyl ions, including those formed from sulphides by hydrolysis. See also the Annex.

The terms *sulphidity* and *degree of causticizing* are explained in the Annex.

3 Principle

A sample of the liquor is titrated with hydrochloric acid of known concentration. The pH value (or a suitable function of the pH value) of the reaction mixture and the volume of hydrochloric acid are recorded continuously and from the recorded data the consumption of acid at the inflexion points is determined.

From the amounts of acid required to reach the three inflexion points, the effective, active and total alkali of the sample are calculated.

4 Apparatus

Automatic titration equipment, including glass and reference electrodes, that records the titration curve (pH against titrant consumed) or any function of the titration curve, such as the first derivative, so that the inflexion points of the titration curve can be determined. The reference electrode should preferably be of the double junction type. Check the precision of the equipment as instructed in Section 6.

Note - For the analysis of green liquors a titration equipment that automatically evaluates the inflexion points is recommended.

5 Reagents

5.1 *Hydrochloric acid*, 1 mol/l, analytical grade. The actual concentration should be known to the nearest 0,005 mol/l.

5.2 *Buffer solutions of known pH values near 4 and 9*. Suitable buffer solutions are commercially available. They can also be prepared in the laboratory as follows: Buffer solution, pH 4,01: In a 1000 ml volumetric flask dissolve 10,12 g of potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$, in distilled water and dilute to the mark. There is normally no need to dry the salt. The solution is stable for 2 months.

Buffer solution, pH 9,18: In a 1000 ml volumetric flask dissolve 3,80 g of sodium tetraborate decahydrate (borax), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, in distilled water from which carbon dioxide has been expelled by boiling. Dilute to the mark. The solution is stable for 6 weeks. The solution will absorb carbon dioxide when in contact with ambient air. Therefore keep the solution in a stoppered bottle and do not leave the bottle open more than is absolutely necessary.

6 Calibration and check of pH meter

Operate the pH meter in accordance with the manufacturer's instructions. Wash the glass and reference electrodes with distilled water; allow the water to drain from the electrodes, but do not wipe them.

Fill a sample cup with the first buffer solution and immerse the electrodes. Adjust the meter so that it indicates the known pH of the buffer solution. If the reading slowly but continuously increases or decreases, this indicates faulty electrodes.

Wash the electrodes with distilled water as before and immerse them in the second standard buffer solution. Do not readjust the meter. The reading should

now agree to within 0,2 pH unit with the value assigned to the buffer. Failure to do so indicates a faulty electrode.

7 Procedure

Operate the titration equipment as instructed by the manufacturer. Use the hydrochloric acid (5.1) as the titrant.

Note - Hydrogen sulphide will be formed during the titration. Since hydrogen sulphide is a toxic gas, the titration should be performed under a hood or other measures should be taken to protect the operator.

Choose the sample volume (v ml) so that about half the burette capacity (or equivalent volume-measuring device) is used. Normally a sample volume of 20 % of the burette capacity is suitable.

With the aid of a calibrated pipette or equivalent device, transfer the chosen volume of sample to the titration vessel. The sample volume should be known with a precision of at least 1 per cent. Dilute the sample with distilled water to a suitable volume. Start the titration and note the volume of acid consumed as follows:

Volume consumed at the first inflexion point:	a ml
Total volume consumed at the second inflexion point:	b ml
Total volume consumed at the third inflexion point:	c ml

Note - Normally the three inflexion points appear at the following pH values:

1st inflexion point	- close to 11
2nd inflexion point	- between 8 and 9
3rd inflexion point	- close to 4

8 Calculation and report

The results may be given in units of substance concentration (moles per litre) or in the conventional way as <<grams of sodium hydroxide per litre>>.

To obtain the results in moles per litre calculate as follows:

Effective alkali	$= a \cdot m/v$
Active alkali	$= (2a - 2b + c) \cdot m/v$
Total alkali	$= c \cdot m/v$

where

m is the concentration of the hydrochloric acid in moles per litre,

v is the volume of sample taken, in millilitres.

If the final results are required in <<grams of sodium hydroxide per litre>>, multiply the above results by 40 (the relative molecular mass of NaOH). For calculation of sulphidity, and degree of causticizing, see the Annex.

Report the results to the nearest 0,01 mol/litre or to the nearest 1g/l.

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

- (a) date and place of testing,
- (b) identification mark of the sample tested,
- (c) the results,
- (d) any departure from the standard procedure and any other circumstances that may have affected the test results.

9 Additional information

Comparison with SCAN-N 2 - A number of different white (69) and green (15) liquors were analysed according to the procedure in this Method and that in SCAN-N 2. There was no significant difference between the two sets of results at the 99% confidence level.

Annex

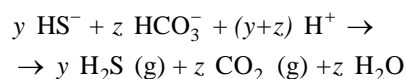
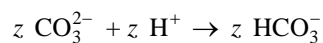
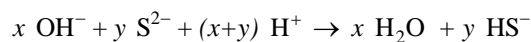
Quantities and units for the characterization of white and green liquors

When the smelt from the recovery furnace in a normal sulphate pulp mill is dissolved in water, the major anionic species formed are OH^- , HS^- and CO_3^{2-} .

The major cationic species are Na^+ and K^+ . The liquor also contains a number of minor constituents, such as SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, Cl^- and many others as traces. Oxidized liquors may also contain significant amounts of polysulphides, *i.e.* ions of the general composition S_nS^{2-} or HS_nS^- .

The analytical procedures described in this Standard and in SCAN-N 2 are based on the assumption that only three anionic species OH^- , HS^- and CO_3^{2-} are present in significant amounts. The presence of other anionic species is thus disregarded. If the concentrations of other species, such as polysulphides and others forming weak acids, rise to a significant level, the above assumption becomes invalid and the properties calculated from the titration procedure lose their meaning.

When the titration curve (pH against acid consumption) is recorded, three inflexion points are obtained. These are considered to be the end points of the reactions:



where

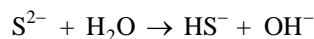
x is the amount of hydroxyl ions

y is the amount of sulphide ions

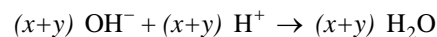
z is the amount of carbonate ions

in the original sample.

In reality no S^{2-} ions are present in white and green liquors because of hydrolysis according to the reaction



This reaction takes place when the smelt is dissolved in water. More correctly, the first reaction in the titration should be written as



The quantity <<effective alkali>> is thus a measure of the total concentration of hydroxyl ions, regardless of whether these are formed by dissolving sodium (or potassium) hydroxide or by hydrolysis of sulphide ions.

The quantity <<active alkali>> is the calculated sum of the concentrations of OH^- and HS^- .

The quantity <<total alkali>> is determined from a titration of all alkaline species, including HCO_3^- ions formed from CO_3^{2-} . Minor concentrations of alkaline constituents other than the main components are also included. Any sulphite ions present are included in the values for total and active alkali.

From acid consumption at the three inflexion points it is possible to calculate the concentrations of the three ionic species OH^- , HS^- and CO_3^{2-} present at the beginning of the titration:

$$a \cdot m = v [\text{OH}^-]$$

$$b \cdot m = v ([\text{OH}^-] + [\text{CO}_3^{2-}])$$

$$c \cdot m = v ([\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HS}^-])$$

which gives

$$[\text{OH}^-] = a \cdot m / v$$

$$[\text{HS}^-] = (a - 2b + c) \cdot m / v$$

$$[\text{CO}_3^{2-}] = (b - a) \cdot m / v$$

The brackets denote amounts of substance concentrations of ionic species. The other symbols are explained in sections 7 and 8.

The concentrations of HS^- and CO_3^{2-} are obtained as the differences between experimentally determined numbers. If the difference is small compared with these numbers, it is markedly influenced by experimental errors. The results for HS^- and CO_3^{2-} , when calculated as indicated, therefore often have a poor precision. This should be borne in mind when such results are used.

Three derived properties are more or less commonly used to describe white and green liquors:

$$\text{Sulphidity} = \frac{2[\text{HS}^-]}{[\text{OH}^-] + [\text{HS}^-]}$$

$$\text{Degree of causticizing} = \frac{[\text{OH}^-] - [\text{HS}^-]}{[\text{OH}^-] - [\text{HS}^-] + 2[\text{CO}_3^{2-}]}$$

$$\text{Degree of reduction} = \frac{[\text{HS}^-]}{[\text{total sulphur}]}$$

These properties are dimensionless quotients and they are normally expressed as percentages.

To calculate the derived properties sulphidity and degree of causticizing the following

$$\text{Sulphidity} = \frac{2(a - 2b + c)}{2a - 2b + c}$$

$$\text{Degree of causticizing} = \frac{2b - c}{4b - 2a - c} = \frac{2b - c}{(2b - c) + 2(b - a)}$$

Note - The rather complicated definition of the degree of causticizing is explained by the old definition:

$$\text{Degree of causticizing} = \frac{[\text{NaOH}]}{[\text{NaOH}] + [\text{Na}_2\text{CO}_3]}$$

which was based on the assumption that white or green liquors are mixtures of dissolved NaOH, Na₂S and Na₂CO₃.

More precise estimates of these quantities may be obtained using values for the sulphide and carbonate concentrations that have been determined separately.

SCAN-test Methods are issued and recommended by KCL, PFI and STFI-Packforsk for the pulp, paper and board industries in Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, SE-114 86 Stockholm, Sweden