



*White and green liquors*

## Total, active and effective alkali

*Titration with indicators*

### 0 Introduction

This revised SCAN-test Method is technically identical with the older version, SCAN-N 2:63. The definitions of the quantities and terms used for the characterization of white and green liquors have been changed to comply with those given in SCAN-N 30.

White and green liquors can be analyzed as described in this Method by traditional titration (using barium chloride precipitation, the formaldehyde reaction and visual end-point detection) or by the titration with potentiometric end-point detection described in SCAN-N 30. The results obtained by the two procedures do not differ significantly.

### 1 Scope and field of application

This SCAN-test Method specifies the details of the traditional titration (with indicators) 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. Nor may it be used for alkaline pulping liquors containing significant amounts of sulphite, such as pulping liquors for sulphite and sulphide-sulphite cooking. 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. See also Section 7, Additional information.

### 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 SCAN-N 30.

Note – See also the Appendix to SCAN-N 30.

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 SCAN-N 30.

Note – In practice active alkali is considered to be the sum of the concentrations of hydroxyl and hydro-sulphite ions, including hydroxyl ions formed by hydrolysis of sulphides. See also the Appendix to SCAN-N 30.

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 in the procedure specified in SCAN-N 30.

*Note* – In practice this is considered to be the concentration of hydroxyl ions, including those formed from sulphides by hydrolysis. See also the Appendix to SCAN-N 30.

Quantities and units used for characterising white and green liquors are discussed in the Appendix to SCAN-N 30.

### 3 Principle

To a measured amount of the liquor, barium chloride solution is added to precipitate the carbonate. Effective alkali is determined by titration with acid to the thymolphthalein end-point (pH 9,5). Formaldehyde is then added to convert the hydrogen sulphide ions to a strong base and active alkali is determined by continuing the titration to the phenolphthalein end-point (pH 8). Finally the titration is continued to the bromophenol blue end-point (pH 4) to give the total alkali.

### 4 Reagents

In the preparation of reagents, use only chemicals of analytical grade and distilled water.

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

4.2 *Barium chloride solution*, 200 g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per litre.

4.3 *Formaldehyde*,  $\text{HCHO}$  about 35 %. Neutralize with about 1 mol/l sodium hydroxide solution to a faint red colour with phenolphthalein as the indicator.

4.4 *Thymolphthalein indicator*, 0,1 %. Dissolve 0,1g in 100 ml of ethanol.

4.5 *Phenolphthalein indicator*, 0,1 %. Dissolve 0,1 g in 100 ml of ethanol.

4.6 *Bromophenolblue indicator*, 0,1 %. Dissolve 0,1 g in 100 ml of distilled water.

### 5 Procedure

Pipette 5,0 ml of the liquor into a 200 ml conical flask. Dilute with about 30 ml of distilled water and add 20 ml of the barium chloride solution (4.2)

*Note* – Since toxic gases may be released, the titration should be performed under a hood, or other measures should be taken to protect the operator.

Titrate immediately with the hydrochloric acid (4.1) from a 25 ml burette, using 0,5 ml of the thymolphthalein solution (4.4) as the indicator. Note the acid consumption at the end-point as  $a$  ml.

Add immediately 5 ml of neutralized formaldehyde solution (4.3), wait for 30 s and titrate to a very faint blue colour. Add 0,5 ml of the phenolphthalein indicator (4.5) and titrate to a faint pink colour. Note the total acid consumption at this point as  $b$  ml.

Add 0,5 ml of bromophenolblue solution (4.6) and continue the titration to the end-point, indicated by a colour change from blue-violet to yellow. Note the total consumption of acid as  $c$  ml.

### 6 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:  $b \cdot m/v$

total alkali:  $c \cdot m/v$

where

$a$  is the consumption of acid to the thymolphthalein end-point, in millilitres,

$b$  is the consumption of acid to the phenolphthalein end-point, in millilitres,

$c$  is consumption of acid to the bromophenol blue end-point, in millilitres,

$m$  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).

Report the results to the nearest 0,01 mol/l or to the nearest 1 g/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 this Method and any other circumstances that may have affected the test results.

## **7 Additional information**

*Comparison with SCAN-N 30* – A number of different white (69) and green (15) liquors were analysed according to the procedure in this Method and that in SCAN-N 30. There was no significant difference at the 99 % confidence level between the two sets of results.

Certain liquors may, however, contain small amounts of sulphites, for example liquors prepared with the use of scrubber liquid for absorbing sulphur dioxide. When analysed as described in this Method such liquors give a slightly lower value for active alkali than when they are analysed according to SCAN-N 30.

The explanation is assumed to be that in the titration, described in SCAN-N 30, sulphite ions, like hydrogen sulphide ions, consume acid at about pH 7. They will therefore be included in total and active alkali, but not in effective alkali. In the titration according to this Method, however, they will be precipitated as barium sulphite and will not react before the final titration to the bromophenol blue end-point. They will thus not be included in the value for active alkali. The results for effective and total alkali will not be affected.