



Black liquor

Residual alkali (Hydroxide ion content)

1 Scope

This SCAN-test Standard describes a procedure for determining the content of residual alkali in kraft black liquors having a dry matter content up to 40 %.

Note – If the dry matter content of the sample exceeds 40 %, the sample needs to be diluted with distilled water to a dry matter content around 20 %.

The method is based on a potentiometric titration with hydrochloric acid and is intended for black liquor samples with an initial pH of at least 11,0.

The lower limit of determination is 0,1 g/l.

2 Reference

SCAN-N 22 Black liquor – Dry matter content

3 Definition

Residual alkali – The content of hydroxide ions that can be determined by potentiometric titration as specified in this Standard. The hydroxide ions can result when sodium (or potassium) hydroxide is dissolved in water and sulphide ions are hydrolysed.

Note 1 – Residual alkali is also called effective alkali, but SCAN-test recommends the former term.

Note 2 – The result is expressed in moles of hydroxide ions per litre of sample or in grams of sodium hydroxide per litre of sample.

4 Principle

The black liquor sample is titrated potentiometrically with hydrochloric acid to the first inflection point, which is situated above pH 11,0 and below 11,5. Before the titration, sodium carbonate is added to the sample to give a better inflection point and to buffer the titration solution. If the initial pH of the black liquor sample is above 11,0 but below 12,5 a known volume of sodium hydroxide must be added to the sample before the titration. The content of residual alkali is calculated from the consumption of the acid at the first inflection point. The result is corrected in order to obtain the true value of the residual alkali content.

5 Reagents

All chemicals must be of analytical grade. The water used in the titration and in the preparation of reagents must be distilled or deionized.

5.1 *Sodium carbonate solution*, $c(\text{Na}_2\text{CO}_3) = 1 \text{ mol/l}$. Dissolve 106,0 g of sodium carbonate, Na_2CO_3 in water and dilute to 1 litre with water.

5.2 *Hydrochloric acid*, $c(\text{HCl}) = 1 \text{ mol/l}$. The actual concentration shall be known to the nearest 0,001 mol/l.

5.3 *Sodium hydroxide solution*, $c(\text{NaOH}) = 1 \text{ mol/l}$. Dissolve 40,0 g of sodium hydroxide in water in a 1 litre volumetric flask and dilute to the mark with water. Check the concentration by titration with a standard acid. The actual concentration shall be known to the nearest 0,005 mol/l.

Note – Commercially available standard solutions may be used.

5.4 *Ethanol* for washing the electrodes.

5.5 *Buffer solutions*, having pH values such as 7,0 and 11,0. Suitable buffer solutions are commercially available or can be prepared as follows:

pH 7,00 , 25 °C:

Dissolve 6,80 g of potassium dihydrogen phosphate (KH_2PO_4), previously dried for 2 hours at 105 °C, and 1,16 g of sodium hydroxide (NaOH) in water in a 1 litre volumetric flask and dilute to the mark.

pH 11,00 , 25 °C:

Dissolve 3,55 g of disodium hydrogen phosphate (Na_2HPO_4), previously dried for 2 hours at 105 °C, and 0,16 g of sodium hydroxide (NaOH) in water in a 1 litre volumetric flask and dilute to the mark.

6 Apparatus

Ordinary laboratory equipment and the following:

6.1 *Automatic titrator or pH-meter*. An automatic device for potentiometric titration including a motorized burette (10 ml) and a recorder are recommended.

6.2 *Electrodes*. Suitable glass and reference electrodes. The reference electrode can be e.g. a calomel electrode. A combined pH glass electrode may also be used.

Note – Wash the electrodes with ethanol (5.4) if the response time deteriorates.

7 Sampling and sample pretreatment

Black liquor is sensitive to oxidation by air. Prevent oxidation by keeping the sample bottles completely filled and tightly closed.

8 Calibration and check of pH meter

Operate the pH meter in accordance with the manufacturer's instructions. Wash the electrodes (6.2) with water; allow the water to drain from the electrodes, but do not wipe them.

Fill the titration vessel with the first standard buffer solution (5.5), measure the temperature of the solution and immerse the electrodes.

The first buffer solution should be chosen so that the pH value of the solution is in the same region as the electric zero point of the pH meter (usually pH = 7).

Adjust the meter so that it indicates the known pH of the first buffer solution at the actual measuring temperature. A slow but continuous increase or decrease in the reading indicates faulty electrodes.

Wash the electrodes with water as before and immerse them in the second standard buffer solution (5.5). The temperature of the second buffer solution should not deviate by more than two degrees from the temperature of the first buffer solution. Adjust the meter, in accordance with the manufacturer's instructions, so that it indicates the known pH of the second buffer solution.

9 Procedure

Run the determination in duplicate. Operate the titration equipment (6.1) as instructed by the manufacturer. Wash the electrodes (6.2) with water, allow the water to drain from the electrodes and insert them in the black liquor sample. Stir with a magnetic stirrer and measure the pH of the sample at least twice. The temperature of the sample should not deviate by more than five degrees from the temperature of the buffer solutions.

9.1 *Warning*. Hydrogen sulphide can 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.

9.2 If the pH is below 11,0 , the sample contains no residual alkali.

9.3 If the pH is above 11,0 but below 12,5 , an addition method must be used. Add approximately 5 ml

NaOH-solution (5.3) to the nearest 0,01 ml to the titration vessel before titration and follow the procedure described below (9.4).

9.4 If the initial pH of the sample is above 12,5 , add 80 ml of water, 10 ml of sodium carbonate solution (5.1) and 10 ml of black liquor in a suitable vessel for titration. The amount of liquor can be reduced or increased, if necessary. In this case the amount of water and sodium carbonate solution shall be adjusted correspondingly.

Insert the electrodes in the solution and stir with a magnetic stirrer. Titrate with hydrochloric acid (5.2) past the first inflection point so that an S-shaped curve is obtained. If an automatic device is not used, read the potentiometric value after each addition and construct the titration curve by plotting each reading against the corresponding total volume of hydrochloric acid (5.2) added. Read the volume of hydrochloric acid at the inflection point (a). If there is no distinct inflection point, read the volume of hydrochloric acid at pH 11,5. This shall then be mentioned in the report.

10 Calculation

Calculate the residual alkali from the expressions:

$$X_1 = \frac{0,95(aC_1 - bC_2)}{V} - 0,012$$

$$X_2 = 40 X_1$$

where

- X_1 is the residual-alkali content of the black liquor expressed as OH^- , in moles per litre;
 X_2 is the residual-alkali content of the black liquor expressed as NaOH, in grams per litre;
 a is the volume of the hydrochloric acid consumed at the first inflection point, in millilitres;
 b is the volume of the sodium hydroxide (5.3) added before the titration (here 5 ml), in millilitres;
 C_1 is the concentration of hydrochloric acid (5.2), moles per litre;
 C_2 is the concentration of sodium hydroxide solution (5.3), in moles per litre;
 V is the volume of the sample, in millilitres;
 40 is the relative molecular mass of NaOH, in grams per mole.

Note 1 – If the value of the residual alkali is negative, then the result is expressed as < 0,1 g/l. The negative value, see *Figure*, indicates the amount of hydrochloric ions needed to titrate weak acids present in the solution.

Note 2 – The correction factor (0,95) and correction term (-0,012) are explained as follows:

The hydroxide ion content, calculated at the first inflection point of the titration gives an overestimated value.

The difference between the measured and true values of the hydroxide ion concentration depends on the acid/base properties of the organic and inorganic substances present in the black liquor. When the titration is performed according to this SCAN-test Standard where the pH-value is in the range 11 to 11,5 , parts of these other species are also titrated. This is not the case when a reference method is used for the determination of the hydroxide ion content, since for this method the pH-range used is > 12,5. Thus the measured value according to this SCAN-test Standard always has to be corrected in order to obtain the true value of the hydroxide ion content.

The correction factors of the residual alkali are based on the report by Ulmgren et al (13.3). The true value of hydroxide ions is calculated by an extrapolation method using data from a potentiometric titration of a sample of the black liquor. According to this reference method the correction equation for all types of black liquors is:

$$\text{True } [\text{OH}^-], \text{ g/l} = 0,95 \cdot \text{measured value} - 0,48$$

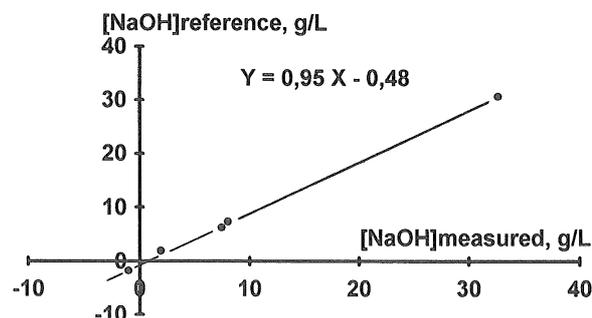


Figure Comparison between the measured NaOH content and the NaOH content, according to the reference method (13.3).

Calculate the mean value of at least two parallel determinations. The results of the parallel determinations should not deviate by more than 5 % from their mean.

11 Report

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

- date and place of testing;
- identification mark of the sampled tested;
- the method of determination used and if relevant a identify the end-point of the titration;
- the measured pH of the sample;
- the result given to two significant figures;
- any departure from the standard procedure and any other circumstances that may have affected

the result.

12 Precision

12.1 Repeatability

Three samples were investigated in one laboratory. Ten parallel determinations were made in each case. The results were as follows:

Residual-alkali content Mean value, g/l	Coeff. of variation, %
3,0	0,55
9,3	0,12
33	0,04

12.2 Reproducibility

Three samples were investigated in four laboratories. The results were as follows:

Residual-alkali content Mean value, g/l	Coeff. of variation, %
2,9	2,0
8,5	4,8
31	0,86

13 Bibliography

13.1 Wilson, K.; Bestämning av effektivt alkali i svartlut. Svensk Papperstid., 71(1968):11, 446-447.

13.2 Milanova, E. and Dorris, G.M.: On the determination of residual alkali in black liquors. Nordic Pulp Paper Res. J., 9(1994):1, 4-9, 15.

13.3 Ulmgren, P., Lindström, R. and Printz, M.: The alkalinity of black liquor. Nordic Pulp Paper Res. J., 9(1994):2, 76-83, 135.

SCAN-test Standards are issued and recommended by the central laboratories of the pulp, paper and board industries in Denmark, Finland, Norway and Sweden.

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