

White, green and black liquors and burnt lime sludge

Carbonate content

0 Introduction

This SCAN-test Method replaces SCAN-N 32:88 from which it differs in that it, in addition to white and green liquors and burnt lime sludge, also makes it possible to determine carbonate ion concentration in black liquors. A high carbonate content increases the risk of precipitation of incrusts (precipitate of calcium carbonate) in boilers or in the evaporation plant.

In the revised method, potassium permanganate has been replaced by buffered silver nitrate as washing solution because it has been observed that all sulphur compounds are no longer absorbed in the potassium permanganate solution when about half of the permanganate ions have been used. The work within SCAN-test has shown that this revised method gives results equivalent to those obtained by the previous version of the Standard (SCAN-N 32:88) with fresh solutions.

An alternative procedure for determining the carbonate ion concentration in white, green and black liquors is also given in Annex A. The procedure, which gives the same result as the revised standard procedure, has been developed by laboratories employing a Total Organic Carbon (TOC) analyser.

1 Scope

This Method describes two different procedures for determining the carbonate content of white, green and black liquors obtained and used in the kraft pulping

process. The determination of carbonate content of burnt lime sludge (burnt lime mud) is also described in one of the procedures.

The lower limit of determination is 5 mmol/l for liquid samples and 20 mmol/kg for solid samples (burnt lime sludge).

In Annex A, a procedure is described based on the measurement of Total Inorganic Carbon (TIC) in liquors.

2 Reference

SCAN-N 22 Black liquor – Dry matter content and fibre content

3 Definition

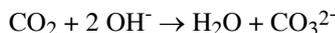
For the purpose of this Method, the following definition applies:

3.1 *Carbonate content* – The total amount of carbonate ions present in white, green and black liquor and in burnt lime sludge.

4 Principle

The sample is treated with hydrochloric acid in a reaction vessel. The carbonates present are decomposed and carbon dioxide as well as some volatile sulphur compounds are released. By means of a carrier gas, the

volatile reaction products are swept through a washing bottle containing buffered silver nitrate solution that absorbs the sulphides. The carbon dioxide passes the washing bottle and is absorbed in an absorption cell containing sodium hydroxide solution:



This reaction leads to a decrease in the electrical conductivity of the absorption solution. The decrease is recorded by a conductance meter. Sodium carbonate standard solutions are used for calibration.

Note – An alternative procedure is described in Annex A.

5 Reagents

5.0 All chemicals must be of analytical grade. Use distilled, carbon-dioxide-free water for the preparation of solutions.

Note 1 – Carbon-dioxide-free water can be prepared from distilled water either by boiling the water for 15 min or by displacing the dissolved air with nitrogen gas.

5.1 *Hydrochloric acid*, $c(\text{HCl})$, approx. 3 mol/l. Add, with caution, 250 ml of hydrochloric acid, HCl, density 1,19 g/cm³, to about 500 ml of distilled water (5.0). Allow to cool and dilute to 1 litre with distilled water.

5.2 *Buffered silver nitrate solution*, $c(\text{AgNO}_3) = 0,1$ mol/l. Dissolve 17 g of dry silver nitrate, AgNO₃, in 800 ml of water (5.0) in a 1000 ml volumetric flask. Add 25 ml of lactic acid, CH₃CH(OH)COOH, and shake the flask, and then add 4,4 g of sodium hydroxide, NaOH, and shake until the colour of the solution has changed to light brown. Dilute to the mark. The pH of the silver nitrate solution is between 3,0 and 3,5.

Note 2 – Commercially available buffered silver nitrate solution may be used.

5.3 *Sodium hydroxide solution*, $c(\text{NaOH}) = 0,1$ mol/l. Dissolve 4,0 g of sodium hydroxide, NaOH, in 1 litre of water (5.0).

Note 3 – Commercially available sodium hydroxide solution may be used.

5.4 *Standard sodium carbonate solution*, $c(\text{Na}_2\text{CO}_3) = 1$ mol/l. Dry sodium carbonate, Na₂CO₃, in an oven for 1 h at 270 °C. Allow to cool in a desiccator. Prepare a portion of the dry salt, weighing exactly 26,498 g, and

transfer it to a 250 ml volumetric flask. Dissolve the salt in water, free from carbon dioxide (5.0), and dilute to the mark with water. The actual concentration shall be known to the nearest 0,001 mol/l. The solution is stable if stored in a closed bottle of polyethylene (PE) or of alkali-resistant glass.

5.5 *Supply of compressed nitrogen as a carrier gas*, capable of maintaining a constant flow (100 ml/min) of nitrogen through the reaction vessel, the washing bottle and the absorption cell.

5.6 *Gelatine capsules*.

6 Apparatus

6.1 *Reaction vessel, gas washing bottle and absorption cell* (an example is shown in *Figure 1*). The reaction vessel has a cold finger that works as a reflux condenser, a gas inlet tube, a thermometer and an injection septum for the introduction of solutions by a syringe. The absorption cell has a water-jacket for circulation of constant-temperature water. It is provided with two platinum electrodes for measuring electrical conductance.

Note – The glass apparatus can be purchased from Werner-Glas AB, Västra Rydsvägen 118, S-19631 Kungsängen, Sweden, or from Laborex Oy, P.O. Box 24, FIN-00880 Helsinki, Finland.

6.2 *Conductometer*, with recorder.

6.3 *Thermostat*, with a pump for circulation of constant-temperature water to the water-jacket of the absorption cell, capable of maintaining the water at a constant temperature, preferably $(25,0 \pm 0,01)$ °C.

6.4 *Electrical heater* for the reaction vessel (6.1).

6.5 *Syringe*, volume between 10 µl and 500 µl, for the injection of solutions through the septum into the reaction vessel.

7 Assembly of the apparatus

Assemble the apparatus and check the flows of cooling and constant-temperature water. Add 50 ml of hydrochloric acid (5.1) to the reaction vessel (6.1), buffered silver nitrate solution (5.2) to the washing bottle and 50 ml of sodium hydroxide solution (5.3) to the absorption cell. The amounts of the solutions can be reduced or increased depending on the size of the vessels. Start the carrier gas stream and adjust it to about (100 ± 10) ml/min. Insert the electrode holder in the absorption cell and connect it to the conductance meter.

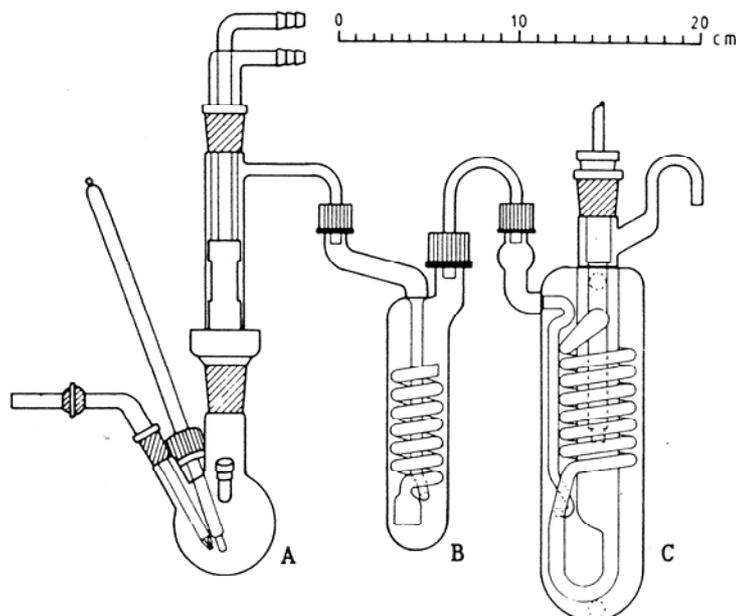


Figure 1. Reaction flask, washing bottle and absorption cell. (A) is the reaction flask with its gas inlet tube, thermometer and septum for a syringe. The reaction flask has two necks, one with a stopper and one for the outlet and the cold finger. (B) is the washing bottle and (C) is the absorption cell with the electrodes mounted on a separate electrode holder inserted through the top opening of the cell.

8 Calibration and maintenance of the apparatus

Heat the reaction vessel with the electrical heater (6.4) until the temperature of hydrochloric acid (5.1) is about 100 °C.

Record the conductance of the absorption solution until it reaches a constant level. Through the septum, add with the syringe (6.5) 100 µl of the standard sodium carbonate solution (5.4). Continue the recording until the recorder reading has again reached a stable level. (This normally takes about 15 min.) Repeat this calibration procedure with other volumes of the standard sodium carbonate solution, for example 150 µl, 50 µl and 10 µl. Read the decrease in conductance in millimetres of recorder or any other suitable unit after each addition of standard carbonate solution, *b*.

Construct a calibration curve by plotting each reading against the corresponding sodium carbonate concentration. The ratio between the volume of carbonate solution and the decrease in conductance should be constant for each absorption solution.

Before and after each determination, the conductance should be constant. A drifting value indicates that the thermostat is incapable of keeping the temperature of the water within the prescribed limits. An unstable conductance value can also indicate faults in the electrical connections to the electrode. A non-linear relation between volume of carbonate and decrease in conductance indicates that the sodium hydroxide solution in the absorption cell is exhausted.

The solutions in the three vessels need not to be renewed after each determination. Normally the same solutions can be used for a whole working day.

After one day's use, empty the reaction vessel, the washing bottle and the absorption cell and clean them. A black coating in the washing bottle consists of silver sulphide; it can be dissolved in nitric acid.

Rinse the apparatus with water followed by acetone. Dry by drawing a current of air through the apparatus.

9 Preparation of sample and procedure

Run the determination in duplicate.

Analyse the liquid sample as taken. Suitable volumes of sample are:

- White liquor	300 µl
- Green liquor	75 µl
- Black liquor	200 µl

Introduce into the reaction vessel liquid samples by means of a graduated syringe.

Weigh solid samples in gelatine capsules (5.6). If required, determine the dry matter content separately. For burnt lime sludge, the amount of sample taken should be selected taking into consideration the anticipated carbonate content.

Bring the apparatus into working order as described in clause 8. When the conductance of the absorption liquid has reached a stable value, add the sample to the reaction vessel.

Introduce gelatine capsules through the glass stoppered inlet of the vessel: Momentarily open the flask and replace the stopper quickly.

Note – Liquid samples such as black liquors can also be weighed and introduced into the reaction vessel in gelatine capsules.

Continue the recording of the conductance until the recorder again shows a constant value. Read the decrease in conductance in millimetres of recorder or any other suitable unit, *a*. The absorption solution has a capacity to absorb about 1,5 mmol of carbonate.

10 Calculation

Use the recorded curves to obtain the calibration factor from the expression:

$$f = \frac{v_1 \cdot c}{b} \quad [1]$$

where

- f* is the calibration factor;
- v*₁ is the volume of standard sodium carbonate solution (5.4), in microlitres;
- c* is the concentration of the standard sodium carbonate solution, in moles per litre;
- b* is the recorded decrease in conductance, in millimetres of recorder deflection or any other suitable unit.

For liquid samples, calculate the concentration of carbonate ions, in moles per litre, from the expression:

$$X = \frac{f \cdot a}{v_2} \quad [2]$$

where

- X* is the carbonate ion concentration of the sample, in moles per litre;
- a* is the recorded decrease in conductance, in the same unit as used for the factor *b*;
- v*₂ is the volume of sample taken, in microlitres.

For solid samples, calculate the carbonate content, in moles per kilogram, from the expression:

$$Y = \frac{a \cdot f}{w} \quad [3]$$

where

- Y* is the carbonate content, i.e. the content of CO₃²⁻, in moles per kilogram;
- w* is the amount of sample taken for analysis, in milligrams.

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

- (a) date and place of testing;
- (b) identification of the sample tested;
- (c) the results to two significant figures;
- (d) any departure from the standard procedure and any other circumstances that may have affected the results.

12 Precision

12.1 *Repeatability*. Samples of white, green and black liquor and burnt lime sludge were investigated in one laboratory. Five parallel determinations were made in each case. The results were as follows:

Sample	Mean value	CV*, %
White liquor	0,48 mol/l	<0,1
Green liquor	1,02 mol/l	<0,1
Black liquor	0,15 mol/l	<0,1
Burnt lime sludge	0,27 mol/kg	4,2

12.2 *Reproducibility*. Samples of white, green and black liquor were investigated in three laboratories. The results were as follows:

Sample	Mean value, mol per litre	CV*, %
White liquor	0,22	0,7
Green liquor	1,24	2,0
Black liquor	0,15	3,2

* CV is the coefficient of variation, i.e. the standard deviation divided by the mean value.

Annex A – Determination of carbonate content using the TIC procedure

A.0 Introduction

This is an alternative procedure using a Total Inorganic Carbon (TIC) procedure for determination of the carbonate content in white, green and black liquors.

A.1 Principle

After dilution in carbon-dioxide-free water, the procedure is based on measurement of Total Inorganic Carbon by a TOC-analyser.

A.2 Reagents

All chemicals must be of analytical grade.

A.2.1 Carbon-dioxide-free water

Note – Carbon-dioxide-free water can be prepared from distilled water either by boiling the water for 15 min or by displacing the dissolved air with nitrogen gas.

A.2.2 *Concentrated standard inorganic carbon solution*, $c(\text{IC}) = 500 \text{ mg/l}$. Dissolve $(2,205 \pm 0,002) \text{ g}$ Na_2CO_3 , previously dried for 1 h at $285 \text{ }^\circ\text{C}$ and $(1,750 \pm 0,002) \text{ g}$ NaHCO_3 , dried over silica gel in a 1000 ml volumetric flask and fill to the mark with water (A.2.1).

A.2.3 *Standard inorganic carbon solutions*, $c(\text{IC}) = 0 \text{ mg/l}$, 10 mg/l , 50 mg/l and 100 mg/l respectively. Transfer 0 ml, 2 ml, 10 ml and 20 ml respectively of the concentrated standard solution (A.2.2) to 100 ml volumetric flasks and fill to the mark with water (A.2.1).

Note – Make the calibration immediately. The diluted solutions keep fresh for one hour.

A.2.4 *Phosphoric acid*, $c(\text{H}_3\text{PO}_4) = 20 \%$. Mix 118 ml 85 % H_3PO_4 with water (A.2.1). Adjust the volume to 500 ml.

A.2.5 *Syringe*, with a filter capsule. The pore size depends on the diameter of the injection needle of the instrument.

A.3 Apparatus

Ordinary laboratory equipment and the following:

A.3.1 Test tubes with lids.

Note – Absorption of carbon dioxide may occur when storing.

A.3.2 *Total Organic Carbon analyser* with auto-sampler. The acid concentration of the IC solution must be at an appropriate level. Regenerate the catalyst and the IC-solution (A.2.3) with phosphoric acid (A.2.4) as instructed by the manufacturer.

A.4 Procedure

Transfer between 0,5 ml and 2 ml of the sample with a syringe to a 100 ml volumetric flask and fill to the mark with water (A.2.1).

If possible, dilute the sample under air-free conditions. Ensure that the glass stopper fits tightly.

If necessary, filter the sample through a filter capsule (A.2.5) to remove particles in the liquor.

The diluted sample must be analysed within 15 min, to prevent absorption of carbon dioxide from the air.

Note – If several samples are to be analysed, a 2 mm layer of paraffin oil can be added on top of the sample solution in each test tube. In this way, the samples can be kept for at least two hours, which is sufficient for the analysis of about 10 samples.

Warning! This procedure cannot be used for samples that are to be analysed for Total Organic Carbon (TOC).

A.5 Analysis

The optimum conditions depend on the apparatus. Use the conditions recommended by the manufacturer.

Perform the calibration with the standard solutions (A.2.3) as instructed by the manufacturer.

A.6 Calculation

Calculate the carbonate ion concentration, in moles per litre, from the expression:

$$X = \frac{C \cdot D}{12 \cdot 1000} \quad [\text{A1}]$$

where

X is the carbonate ion concentration of the sample, in moles per litre;

C is the total amount of inorganic carbon, in milligrams per litre;

D is the dilution factor;

12 is the relative atomic mass of C;

1000 is the factor to convert millimoles to moles.

Calculate the carbonate ion concentration, in grams per litre, according to the equation:

$$X_2 = \frac{C \cdot D \cdot 5}{1000} \quad [A2]$$

where

X_2 is the carbonate ion concentration of the sample, in grams per litre;

C is the total amount of inorganic carbon, in milligrams per litre;

D is the dilution factor;

5 is the numerical factor to convert carbon to carbonate ion (60/12);

1000 is the factor to convert milligram to gram.

The results of the parallel determinations should not deviate by more than 5 % from their mean.

A.7 Report

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

- (a) date and place of testing;
- (b) identification of the sample tested;
- (c) the result to two significant figures;
- (d) any departure from the standard procedure and any other circumstances that may have affected the result.

A.8 Precision

A.8.1 *Repeatability*. One laboratory analysed three different liquors five times. The results were as follows:

Sample	Mean value, mol per litre	CV*, %
White liquor	0,33	1,3
Green liquor	1,45	1,3
Black liquor	0,20	0,7

A.2.2 *Reproducibility*. Three samples were analysed in five laboratories. The results were as follows:

Sample	Mean value, mol per litre	CV*, %
White liquor	0,25	5,1
Green liquor	1,23	3,1
Black liquor	0,17	7,4

* CV is the coefficient of variation, i.e. the standard deviation divided by the mean value.