SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

**SCAN-N 31:94**
Revised 1994

*White, green and black liquor*

# Hydrogen sulphide ion concentration

## 0 Introduction

This SCAN-test Standard replaces SCAN-N 31:85 from which it differs in that it also makes it possible to determine hydrogen sulphide ion concentration i black liquors. To avoid the hazardous handling of mercury-containing chemicals in laboratories, SCAN-test has decided not to use the potentiometric titration with tetrachloromercurate solution for the determination but to use silver nitrate solution.

The work within SCAN-test has shown that potentiometric titration with silver nitrate solution gives results equivalent to those obtained by titration with tetrachloromercurate solution (cf Appendix).

## 1 Scope

This Standard describes a procedure for the determination of sulphide, i.e. the hydrogen sulphide ion concentration, in white and green liquors as well as in black liquor having a dry matter content up to 40 %. The determination also includes the sulphide part of any polysulphide present in the solution.

*Note 1* – If the dry matter content of the sample exceeds 40 %, the sample needs to be diluted with oxygen-free water (5.1) to a dry matter content around 20 %. The procedure can result in low results due to unintentional oxidation during the dilution.

*Note 2* – The Standard has not yet been tested for oxidized white and black liquors.

The Standard is applicable for hydrogen sulphide ion concentrations from 0,02 mol per litre to 2 mol per litre, provided that the volume of the original sample taken to analysis is selected accordingly.

## 2 References

SCAN-N 22 Black liquor – Dry matter content

## 3 Definitions

For the purpose of this Standard the following definitions apply.

3.1 *Hydrogen sulphide ion concentration* – The concentration of $HS^-$ ions in white, green or black liquor.

*Note 1* – Practically no $S^{2-}$ ions are present in white, green and black liquors because of hydrolysis according to the reaction:

$$S^{2-} + H_2O \rightarrow HS^- + OH^- \qquad [1]$$

3.2 *Sulphidity* – The ratio of the concentration of hydrogen sulphide ions to the mean sum of the concentrations of hydroxyl and hydrogen sulphide ions:

$$\text{Sulfidity} = \frac{2c(HS^-)}{c(OH^-)+c(HS^-)}$$

*Note 2* – The derived property sulphidity is often used to describe white and green liquors. The property is a dimensionless quotient and is normally expressed as a percentage.

## 4 Principle

The procedure is based on potentiometric titration with silver nitrate solution:

$$HS^- + OH^- + 2Ag^+ \rightarrow Ag_2S_{(\text{black ppt})} + H_2O \qquad [2]$$

$$CH_3S^- + Ag^+ \rightarrow AgCH_3S_{(\text{yellow ppt})} \qquad [3]$$

Sulphite ions are added to the sample solution in order to dissolve any polysulphide ions that are present:

$$nSO_3^{2-} + S_nS^{2-} + H_2O \rightarrow nS_2O_3^{2-} + HS^- + OH^- \qquad [4]$$

Each polysulphide ion thus contributes one sulphide ion to the sulphide content. As the titration is performed in alkaline solution, thiosulphate or sulphite ions do not interfere in the determination.

## 5 Reagents

5.1 All chemicals must be of analytical grade. Use oxygen-free water for the preparation of the solutions.

*Note* – Oxygen-free water can be prepared from distilled water either by boiling the water for 15 min or by displacing the oxygen with nitrogen gas.

5.2 *Silver nitrate*, $c(AgNO_3)$ = 0,1 mol/l. Dissolve 17 g of dry silver nitrate, $AgNO_3$, in a 1000 ml volumetric flask. Stir and fill up to the mark with water (5.1). Determine the concentration in the following way:

Weigh approximately 750 mg of dried potassium chloride, KCl, to an accuracy of 0,5 mg into a 100 ml volumetric flask, and fill up to the mark with water (5.1). With a precision pipette, take 5 ml for titration in distilled water. Titrate with the silver nitrate solution to the first inflection point. From the silver nitrate consumption, *a* ml, calculate the silver nitrate concentration in moles per litre to four decimal places.

Calculate the silver nitrate concentration, $c(AgNO_3)$, in mol per litre, as follows:

$$c(AgNO_3) = \frac{5 \times b}{a \times 100 \times 74,5513} \qquad [5]$$

where

*a* is the silver nitrate consumption, in millilitres;
*b* is the amount of potassium chloride weighed, in milligrams;
74,5513 is the relative molecular mass of KCl.

Store the silver nitrate solution in a dark glass bottle.

Commercially available solutions of silver nitrate may be used.

5.3 *Sodium hydroxide solution*, $c$(NaOH) approx. 1 mol/l. Dissolve 40 g of NaOH in 1 litre of water (5.1).

5.4 *Alkaline sodium sulphite solution*, $c(Na_2SO_3)$ = approximately 0,5 mol/l. Dissolve 60 g of sodium sulphite, $Na_2SO_3$ and 40 g of sodium hydroxide, NaOH, in 1 litre of water (5.1).

5.5 *Ammonia,* (approx. 25 % $NH_3$).

## 6 Apparatus

6.1 *Automatic titration equipment*. An automatic device for potentiometric titration including a motorized burette (e.g. 10 or 20 ml) and a recorder.

6.2 *Indicator electrode*, a polished silver rod. When it is apparent that the reagents have affected the silver electrode, it shall be cleaned using ordinary silver polish. Store the electrode in a dry place when not in use.

6.3 *Reference electrode*, a calomel electrode.

Check the indicator electrode (6.2) and the reference electrode (6.3) regularly. This can be done by measuring the potential of a mixture of sodium hydroxide (5.3) and ammonia (5.5) solution. The potential should be approximately -200 mV. After sulfide ion solution is added, the potential drops to -800 mV to -900 mV. Replace faulty electrodes.

6.4 *Syringe*, volume 1 ml and/or 2 ml, calibrated.

## 7 Pre-treatment of sample

White, green and black liquors are sensitive to oxidation by air. Prevent oxidation by keeping the sample bottles filled to the rim and tightly closed.

Most white and green liquors as well as black liquors contain small amounts of polysulphide. In order to dissolve the sulphide part of the polysulphide, pretreat the sample according to the following procedure:

Heat a portion of about 10 ml alkaline sodium sulphite solution (5.4) to 80 to 90 °C. With the calibrated syringe (6.4), add an exactly known volume (1 ml to 2 ml) of the sample. Wait 2 to 3 min until the reaction [4] is complete.

*Note 1*– Only when it has been ascertained that no polysulphide is present in the samples to be analysed, may the pre-treatment be omitted. Check for the presence of polysulphides by running portions of the same sample with and without pre-treatment. If no polysulphide is present the shape of the titration curve (see Clause 8, Note 4) should be unaffected by the pre-treatment.

*Note 2* – The polysulphide content in white, green and black liquors is normally low, which means that no pre-treatment is normally necessary.

## 8 Procedure

Run the pretreatment and the titration procedures in duplicate.

To the pretreated sample add approximately 40 ml of sodium hydroxide solution (5.3) and 5 ml ammonia (5.5).

If the pretreatment has been omitted, increase the volume of sodium hyroxide solution to 50 ml.

*Note 1* – The addition of ammonia results in a more flocculated precipitate which makes the inflection point easier to estimate.

*Note 2* – No cooling of the pre-treated sample is required. The waiting time and the dilution of the sample solution with sodium hydroxide solution is sufficient.

The volume of black liquor sample taken to analysis can be decreased or increased, if necessary. In this case, the amount of sodium hydroxide solution should be adjusted correspondingly.

*Titration*. Operate the titration equipment (6.1) as instructed by the manufacturer.

Insert the electrodes (6.2 and 6.3) in the sample solution and stir vigorously to prevent precipitated silver sulphide from sticking to the electrodes. Titrate with the silver nitrate solution (5.2) past the first inflection point so that an S-shaped curve is obtained. Read off the volume (*a* ml) of the silver nitrate solution consumed at the first inflection point.

The inflection point is generally found at a cell potential of –650 mV. If the inflection point is difficult to locate, the consumption at –650 mV may be used instead. This shall then be mentioned in the report.

*Note 3* – Two inflection points can be obtained in a pre-treated black liquor sample. The first inflection point corresponds to hydrogen sulphide ($HS^-$) as described by reaction [2] and the second inflection point corresponds to methyl mercaptan ($CH_3SH$) as described by [3]. The concentration of methyl mercaptan is obtained from the difference in consumed volume between the two inflection points. If the difference is small it is markedly influenced by experimental errors. The result for methyl mercaptan calculated as indicated therefore often has a poor precision. This should be borne in mind when such results are used.

*Note 4* – Two inflection points obtained in the titration of a sample which has not been pre-treated means in most cases disturbance from polysulphide, *Figure 1*. Note that neither of the inflection points in that case gives the correct hydrogen sulphide concentration.

*Note 5* – Sulphite does not interfere in the potentiometric titration. Due to the high pH-level, chloride does not disturb the titration either.

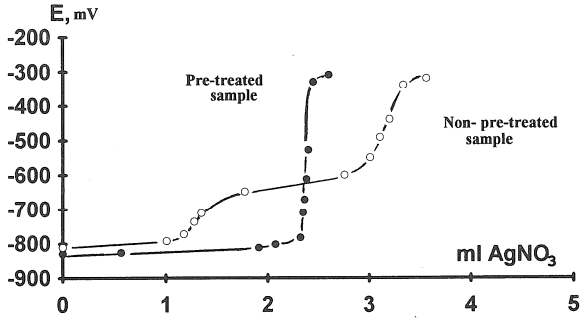


*Figure 1. Titration curves for pre-treated sample and non-pre-treated sample. If the non-pre-treated sample gives two inflection points, the result must be rejected and pre-treatment must be done before a new titration is carried out.*

## 9 Calculation

9.1 Calculate the $HS^-$-concentration in moles per litre from the equation:

$$X_1 = \frac{C \times a}{2\,V}$$

where

$X_1$ is the $HS^-$-ion content of the sample, in mol per litre;
$C$ is the concentration of the silver nitrate solution (5.2), in mol per litre;
$a$ is the volume of the silver nitrate solution consumed at the first inflection point, in millilitres;
$V$ is the volume of the original sample taken, in millilitres.

Calculate the mean value of the parallel determinations and report the result to three decimal places.

9.2 Calculate the $HS^-$-ion content in grams of sulphur per litre according to the equation:

$$X_2 = 32\,X_1$$

where

$X_2$ is the $HS^-$-content of the sample, in grams of sulphur per litre;
32 is the relative atomic mass of S.

Calculate the mean value of the two parallel determinations and report the result to two decimal places. The result of the parallel determinations should not deviate by more than 5 % from their mean.

## 10 Report

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

a) date and place of testing;
b) precise identification of the sample;
c) if relevant, a statement that the pre-treatment has been omitted;
d) if relevant, a statement that the –650 mV cell potential has been used to identify the endpoint of the titration;
e) the test result;
f) any departure from the standard procedure and any other circumstances that may have affected the result.

## 11 Precision

11.1 *Repeatability*. One laboratory tested one white liquor, one green liquor and two different black liquors. Ten parallel determinations were made in each case. The results were as follows:

| Sample | $c(HS^-)$ at the 1st inflection point | | $c(HS^-)$ at -650 mV cell potential | |
|---|---|---|---|---|
| | mean mol/l | CV % | mean mol/l | CV % |
| White liquor | 0,766 | 0,16 | 0,765 | 0,12 |
| Green liquor | 0,740 | 0,06 | 0,740 | 0,05 |
| Black liquor 1 | 0,034 | 0,62 | 0,033 | 1,29 |
| Black liquor 2 | 0,151 | 0,68 | 0,151 | 0,55 |

CV is the coefficient of variation calculated from the mean values.

11.2 *Reproducibility*. One white liquor, one green liquor and four black liquors were analysed in five laboratories. The results were as follows:

| Sample | $c(HS^-)$ at the 1st inflection point | |
|---|---|---|
| | mean mol/l | CV % |
| White liquor | 0,761 | 1,4 |
| Green liquor | 0,733 | 1,2 |
| Black liquor 1 | 0,051 | 4,7 |
| Black liquor 2 | 0,050 | 8,8 |
| Black liquor 3 | 0,218 | 1,6 |
| Black liquor 4 | 0,198 | 3,7 |

## 12 Bibliography

Tappi T 625 cm-85 - Analysis of soda and sulfate black liquor
Chiu, S-t and Paszner, L. - Potentiometric titration of sodium sulphide and methyl mercaptan in sulphate pulping black liquors, Analytical Chemistry *47* (1975): 12, 1910

# Annex –

# Comparison between potentiometric titration methods

The white, green and black liquors used in the reproducibility study, were also analysed by five laboratories using potentiometric titration with tetrachloromercurate solution. The results were as follows:

(The results obtained using silver nitrate are shown for comparison):

| Sample | Titration with tetrachloromercurate $c(HS^-)$ at the 1st inflection point | | Titration with silver nitrate $c(HS^-)$ at the 1st inflection point | |
|---|---|---|---|---|
| | mean mol/l | CV % | mean mol/l | CV % |
| White liquor | 0,753 | 1,7 | 0,761 | 1,4 |
| Green liquor | 0,727 | 1,5 | 0,733 | 1,2 |
| Black liquor 1 | 0,054 | 6,2 | 0,051 | 4,7 |
| Black liquor 2 | 0,054 | 10,5 | 0,050 | 8,8 |
| Black liquor 3 | 0,215 | 3,0 | 0,218 | 1,6 |
| Black liquor 4 | 0,198 | 3,4 | 0,198 | 3,7 |

CV is the coefficient of variation calculated from the mean values.

**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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