

## *Oxidized white liquors*

# Hydrogen sulphide ion concentration

## 0 Introduction

This SCAN-test Standard is an extension of SCAN-N 31:94 making it possible to determine the hydrogen sulphide ion concentration in oxidized white liquors. To avoid the hazardous handling of mercury-containing chemicals, SCAN-test has decided not to permit the potentiometric titration with tetrachloromercurate solution, but to prescribe the use of 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. SCAN-N 31:94, Annex).

## 1 Scope

This Standard is applicable for the estimation of the extent of oxidation of the white liquor.

The Standard describes a procedure for the determination of sulphide, i.e. the hydrogen sulphide ion concentration, in oxidized white liquors. The determination also includes the sulphide part of any polysulphide present in the solution.

*Note 1* – The determination should be made as soon as possible after the sampling to prevent further oxidation.

*Note 2* – The method has not yet been tested for use with oxidized black liquors.

The Standard is applicable to hydrogen sulphide ion concentrations from 0,5 mmol per litre to 50 mmol per litre, provided that the volume of the original sample taken to analysis is selected accordingly. For hydrogen sulphide ion concentrations exceeding 50 mmol per litre, SCAN-N 31:94 can be used.

## 2 Reference

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## 3 Definition

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

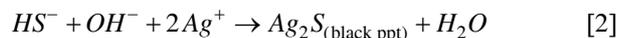
3.1 *Hydrogen sulphide ion concentration* – The concentration of HS<sup>-</sup>-ions in oxidized white liquor.

*Note 1* – Practically no S<sup>2-</sup>-ions are present in oxidized white liquor because of hydrolysis according to the reaction:



#### 4 Principle

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

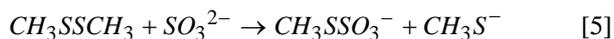


Sulphite ions are added to the sample solution in order to dissolve any polysulphide ions that may be present:



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

When sulphite ions are added to organic polysulphides, mercaptide ions are produced:



#### 5 Reagents

All chemicals must be of analytical grade.

##### 5.1 Oxygen-free water.

*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*,  $c(\text{AgNO}_3) = 10 \text{ mmol/l}$ . Dissolve 1,70 g of dry silver nitrate,  $\text{AgNO}_3$ , in a 1000 ml volumetric flask. Stir and fill up to the mark with oxygen-free water (5.1). Determine the concentration in the following way:

Weigh approximately 750 mg of dried potassium chloride,  $\text{KCl}$ , to an accuracy of 0,5 mg into a 1000 ml volumetric flask and fill up to the mark with oxygen-free water (5.1). With a precision pipette, take 5 ml for titration in oxygen-free water (5.1). Titrate with the silver nitrate solution to the first inflection point. From the silver nitrate consumption,  $a$  ml, calculate the silver nitrate concentration,  $c(\text{AgNO}_3)$ , in millimoles per litre, as follows:

$$c(\text{AgNO}_3) = \frac{5 \cdot b}{74,5513 \cdot a} \quad [6]$$

where

$a$  is the silver nitrate consumption, in millilitres;  
 $b$  is the amount of the potassium chloride

weighed, in milligrams;  
 74,5513 is the relative molecular mass of  $\text{KCl}$ .

Store the silver nitrate solution in a dark glass bottle.

Commercially available silver nitrate solutions may be used.

5.3 *Sodium hydroxide solution*,  $c(\text{NaOH})$ , approx. 1 mol/l. Dissolve 40 g of  $\text{NaOH}$  in 1 litre of oxygen-free water (5.1).

5.4 *Alkaline sodium sulphite solution*,  $c(\text{Na}_2\text{SO}_3) =$  approx. 0,5 mol/l. Dissolve 60 g of sodium sulphite,  $\text{Na}_2\text{SO}_3$  and 40 g of sodium hydroxide,  $\text{NaOH}$ , in 1 litre of oxygen-free water (5.1).

5.5 *Ammonia* (approx. 25 %  $\text{NH}_3$ ).

#### 6 Apparatus

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

6.2 *Indicator electrode*, a polished silver rod. When it is apparent that the reagents have affected the silver electrode, clean it 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 solution (5.5) (see clause 8). The potential should be approx. -200 mV. After the sulphide ion solution has been added, the potential drops to between -800 mV and -900 mV. Replace faulty electrodes.

6.4 *Syringe*, volume 1 ml, 2 ml or 5 ml, calibrated.

#### 7 Pre-treatment of sample

Most of the oxidized white 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 20 ml to 30 ml of alkaline sodium sulphite solution (5.4) to 100 °C. With the calibrated syringe (6.4), add an exactly known volume (between 1 ml and 5 ml) of the sample. Heat the mixture to 100 °C once again. Wait 5 min until reactions [4] and [5] are complete.

*Note* – Only when it has been ascertained that no polysulphide is present in the samples may the pre-treatment be omitted. Polysulphides in the oxidized white liquor give the liquor a yellow colour.

## 8 Procedure

Run the pretreatment and the titration procedures in duplicate.

To the pretreated sample, add approximately 50 ml of sodium hydroxide solution (5.3) and 5 ml of ammonia (5.5).

If the pretreatment has been omitted, increase the volume of sodium hydroxide solution to 70 ml.

*Note 1* – The addition of ammonia will result in a more flocculated precipitation 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.

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

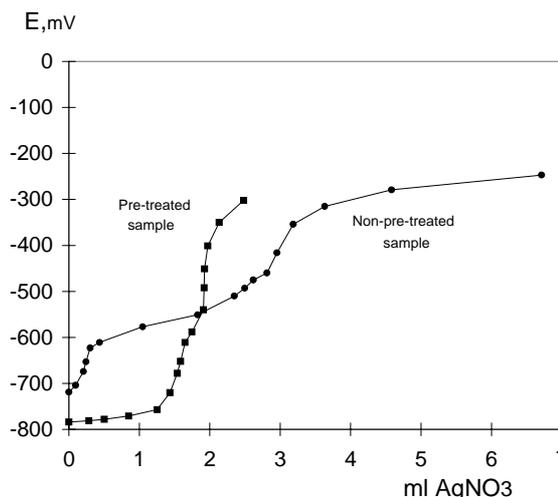
Insert the electrodes (6.2 and 6.3) into the sample solution and stir vigorously to prevent precipitated silver sulphide from sticking to the electrodes. Titrate past the first inflection point with the silver nitrate solution (5.2) so that an S-shaped curve is obtained. Read off the volume,  $a$  ml,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

*Note 3* – In a pre-treated oxidized white liquor sample, two inflection points can be obtained. The first inflection point at approx. -650 mV corresponds to hydrogen sulphide ( $\text{HS}^-$ ), as described by reaction [2]. The second inflection point at approx. -450 mV corresponds to methyl mercaptan ( $\text{CH}_3\text{SH}$ ), as described by reaction [3]. The concentration of methyl mercaptan is obtained from the difference in consumed volume between the two inflection points. The difference is small and it is markedly influenced by experimental errors. The result therefore has a poor precision. If such results are reported, this should be borne in mind.

*Note 4* – The occurrence of two inflection points in the titration of a sample which has not been pre-treated usually means disturbance from polysulphide, *Figure 1*. Note that neither of the inflection points in that case give 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 and non-pre-treated samples. If the non-pre-treated sample gives two inflection points, the result must be rejected and the sample must be pre-treated before a new titration is carried out.

## 9 Calculation

9.1 Calculate the  $\text{HS}^-$ -concentration in millimoles per litre according to the equation:

$$X_1 = \frac{C \cdot a}{2V} \quad [7]$$

where

$X_1$  is the  $\text{HS}^-$ -ion content of the sample, in millimoles per litre;

$C$  is the concentration of the silver nitrate solution (5.2), in millimoles 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 two decimal places.

9.2 Calculate the  $\text{HS}^-$ -ion content in milligrams of sulphur per litre according to the equation:

$$X_2 = 32 X_1 \quad [8]$$

where

$X_2$  is the HS<sup>-</sup>-content of the sample, in milligrams 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 one decimal place. The result of the parallel determinations should not deviate by more than 10 % from each other.

## 10 Report

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

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

## 11 Precision

11.1 *Repeatability*. One laboratory tested two oxidized white liquors. Five parallel determinations were made. The results were as follows:

Sample	c(HS <sup>-</sup> ) at the 1st inflection point		c(HS <sup>-</sup> ) at -650 mV cell potential	
	mean mmol/l	CV %	mean mmol/l	CV %
Oxidized white liquor 1	29,5	1,2	29,6	1,2
Oxidized white liquor 2	1,26	1,9	1,09	1,7

CV is the coefficient of variation calculated with respect to the mean values.

11.2 *Reproducibility*. One oxidized white liquor was analysed in seven laboratories. The results were as follows:

Sample	c(HS <sup>-</sup> ) at the 1st inflection point	
	mean mmol/l	CV %
Oxidized white liquor	3,26	6,5

## 12 Literature

12.1 SCAN-N 31:94 – White, green and black liquor – Hydrogen sulphide ion concentration

**SCAN-test Standards are issued and recommended by the central laboratories of the pulp, paper and board industries in Denmark, Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-114 86 Stockholm, Sweden.**