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Pulps — Kraft liquor — Determination of hydrosulphide ion concentration using potentiometric titration

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Contents

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This document was prepared by Technical Committee ISO/TC *6*, *Paper, board and pulps*.

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Pulps — Kraft liquor — Determination of hydrosulphide ion concentration using potentiometric titration

1 Scope

This document describes a procedure for the determination of sulphide, i.e. the hydrosulphide ion concentration, in white, oxidized 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.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at ~~https://www.iso.org/obp~~https://www.iso.org/obp

— IEC Electropedia: available at ~~https://www.electropedia.org/~~https://www.electropedia.org/

3.1
hydrosulphide ion concentration
concentration in white, black and green liquors or oxidized white liquor

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

~~$S^{2-} + H_2O \rightarrow HS^- + OH^-$~~

$S^{2-} + H_2O \rightarrow HS^- + OH^-$ Field Code Changed

4 Principle

The procedure is based on potentiometric titration with silver nitrate solution according to reaction (1) and (2):

~~$HS^- + OH^- + 2Ag^+ \rightarrow Ag_2S_{(black\ ppt)} + H_2O$~~ $HS^- + OH^- + 2Ag^+ \rightarrow Ag_2S_{(black\ ppt)} + H_2O$ (1) Field Code Changed

~~$CH_3S^- + Ag^+ \rightarrow AgCH_3S_{(yellow\ ppt)}$~~ $CH_3S^- + Ag^+ \rightarrow AgCH_3S_{(yellow\ ppt)}$ (2) Field Code Changed

Sulphite ions are added to the sample solution in order to dissolve any polysulphide ions that are present according to reaction (3):

$$nSO_3^{2-} + S_nS^{2-} + H_2O \rightarrow nS_2O_3^{2-} + HS^- + OH^- \quad (3)$$

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.

When sulphite ions are added to organic polysulphides, mercaptide ions are produced according to reaction (4):

$$CH_3SSCH_3 + SO_3^{2-} \rightarrow CH_3SSO_3^- + CH_3S^- \quad (4)$$

For white, green and black liquor, this document is applicable for hydrosulphide 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. For oxidized white liquors the standard is applicable to hydrosulphide 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.

Precision data are available in Annex A.

5 Reagents

All chemicals shall be of analytical grade.

5.1 Water

Use, 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.

5.1 5.2 Silver nitrate 0,1 M

Dissolve, dissolve 17,0 g of dry silver nitrate, $AgNO_3$, in a 1 000 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, $[AgNO_3]$, in mol per litre, according to Formula (5):

$$[AgNO_3] = \frac{5*b}{74{,}5513*a*100} \quad (5)$$

where

a is the silver nitrate consumption, in millilitres;

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- *b* is the amount of potassium chloride weighed, in milligrams;
- 74,~~5513~~5 is the relative molecular mass of KCl.
  51 3

Store the silver nitrate solution in a dark glass bottle. Commercially available solutions of silver nitrate may be used.

~~5.2~~ 5.3 Sodium hydroxide solution 1- M

~~Dissolve,~~ dissolve 40,0 g of NaOH in 1,0 litre of oxygen-free water (5.1).

~~5.3~~ 5.4 Alkaline sodium sulphite solution approximately 0,5- M

~~Dissolve,~~ dissolve 60,0 g of sodium sulphite, Na_2SO_3 and 40,0 g of sodium hydroxide, NaOH, in 1,0 l of oxygen-free water (5.1).

~~5.4~~ 5.5 Ammonia

~~Approx.,~~ approximately 25- % NH_3.

6 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

~~6.1~~ 6.1 Automatic titration equipment

~~An,~~ an automatic device for potentiometric titration including a motorized burette (e.g. 10- ml or 20 ml) and a recorder.

NOTE If necessary, a manual titrator and a separate pH meter can be used.

~~6.2~~ 6.2 Indicator electrode

~~A,~~ 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~~ 6.3 Reference electrode

~~Check,~~ 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 shall be approximately -200 mV. After sulphide ion solution is added, the potential drops to -800 mV to -900 mV. Replace faulty electrodes.

Type of reference electrode shall be according to the recommendation of the equipment supplier.

~~6.4~~ 6.4 Pipette

~~Volume,~~ volume 1 ml, 2 ml or 5 ml, calibrated.

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7 Sampling and sample pretreatment

7.1 General

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

Most white, oxidized white and green liquors as well as black liquors contain small amounts of polysulphide. The presence of polysulphide in oxidized sample would disturb the dosage and led to two inflection points, that neither give the correct hydrosulphide concentrations. In that case, a pre-treatment of the sample shall be performed.

In order to dissolve the sulphide part of the polysulphide, pre-treat the sample according to the following relevant procedure:

7.2 White, green and black liquors

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

NOTE 1 Pre-treatment is usually not needed except in the cases of oxidized white liquors.

NOTE 2 Usually the sample volume is 0,20 ml to 2 ml.

7.3 Oxidized white liquors

Heat a portion of about 30 ml of alkaline sodium sulphite solution (5.4) to 100 °C. With the calibrated pipette (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 (3) and (4) are complete.

NOTE Only when it has been ascertained that no polysulphide is present in the samples to be analysed, can 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~~ 8.4, Note 2) is unaffected by the pre-treatment. Polysulphides in the oxidized white liquor give the liquor a yellow colour.

8 Procedure

8.1 General

Ensure that the sample in the sample bottle is properly homogenized before the sample is extracted. The samples shall be swirled and not shaken to avoid the effects of oxygen on the sample.

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.

With the aid of a calibrated pipette or equivalent device, transfer the chosen volume of sample to the titration vessel. The sample volume shall be known with a precision of at least 1 per cent.

Run the pre-treatment and the titration procedures in duplicate.

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