

2022-10-17 ~~11-25~~

ISO/FDIS 23777:2022(E)

Secretariat: SCC

ISO TC 6/WG 17

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

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23777

<https://standards.iteh.ai/catalog/standards/sist/a81ebc01-93cf-4f69-a24a-4a0abd00376f/iso-23777>

~~Edited DIS - MUST BE USED FOR FINAL DRAFT~~

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23777
<https://standards.iteh.ai/catalog/standards/sist/a81ebc01-93cf-4f69-a24a-4a0abd00376f/iso-23777>

© ISO 2022

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office

CP 401 • Ch. de Blandonnet 8

CH-1214 Vernier, Geneva

Phone: +41 22 749 01 11

Fax: +41 22 749 09 47

Email: copyright@iso.org

Website: www.iso.org

Published in Switzerland

STANDARD PREVIEW
(standards.iteh.ai)

ISO 23777

<https://standards.iteh.ai/catalog/standards/sist/a81ebc01-93cf-4f69-a24a-4a0abd00376f/iso-23777>

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

© ISO 2022 – All rights reserved

© ISO 2022 – All rights reserved

Contents

Foreword..... iv

1 Scope..... 1

2 Normative references..... 1

3 Terms and definitions..... 1

4 Principle..... 2

5 Reagents..... 2

5.1 General..... 2

5.2 Silver nitrate 0,1 M..... 2

5.3 Sodium hydroxide solution 1 M..... 3

5.4 Alkaline sodium sulphite solution approximately 0,5 M..... 3

5.5 Ammonia..... 3

6 Apparatus..... 3

6.1 General..... 3

6.2 Automatic titration equipment..... 3

6.3 Indicator electrode..... 3

6.4 Reference electrode..... 3

6.5 Pipette..... 3

7 Sampling and sample pretreatment..... 4

7.1 General..... 4

7.2 White, green and black liquors..... 4

7.3 Oxidized white liquors..... 4

8 Procedure..... 4

8.1 White, green and black liquors..... 4

8.2 Oxidized white liquors..... 5

8.3 Titration..... 5

9 Calculation..... 6

10 Report..... 7

Annex A (informative) Precision data..... 8

Bibliography..... 9

Foreword..... iv

1 Scope..... 1

2 Normative references..... 1

3 Terms and definitions..... 1

4 Principle..... 2

5 Reagents..... 2

5.1 General..... 2

5.2 Silver nitrate 0,1 M..... 2

5.3 Sodium hydroxide solution 1 M..... 3

5.4 Alkaline sodium sulphite solution approximately 0,5 M..... 3

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

5.5	Ammonia	3
6	Apparatus.....	3
6.1	General.....	3
6.2	Automatic titration equipment.....	3
6.3	Indicator electrode	3
6.4	Reference electrode.....	3
6.5	Pipette.....	3
7	Sampling and sample pretreatment.....	4
7.1	General.....	4
7.2	White, green and black liquors	4
7.3	Oxidized white liquors.....	4
8	Procedure	4
8.1	White, green and black liquors	4
8.2	Oxidized white liquors.....	5
8.3	Titration	5
9	Calculation	6
10	Report	7
	Annex A (informative) Precision data	8
	Bibliography	9

STANDARD PREVIEW
(standards.iteh.ai)

ISO 23777

<https://standards.iteh.ai/catalog/standards/sist/a81ebc01-93cf-4f69-a24a-4a0abd00376f/iso-23777>

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

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:

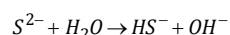
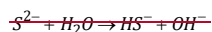
- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

hydrosulphide ion concentration

concentration in white, black and green liquors or oxidized white liquor

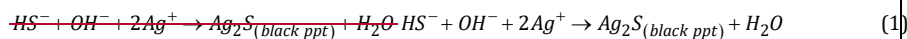
Note 1 to entry: Practically no S^{2-} ions are present in white, oxidized white, green, and black liquors because of hydrolysis according to the reaction:



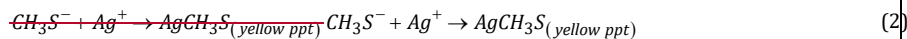
Field Code Changed

4 Principle

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

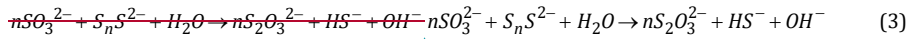


Field Code Changed



Field Code Changed

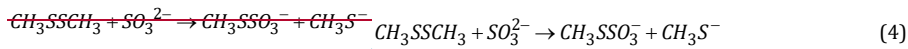
Sulphite ions are added to the sample solution in order to dissolve any polysulphide ions that are present according to reaction-(3):



Field Code Changed

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~~ reaction (4):



Field Code Changed

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.

5.1.2 Silver nitrate 0,1-M

~~Dissolve, dissolve~~ 17,0 g of dry silver nitrate, AgNO₃, 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, [AgNO₃], in mol-per/litre, according to Formula-(5):

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

Field Code Changed

where

- a is the silver nitrate consumption, in millilitres;

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

- b is the amount of potassium chloride weighed, in milligrams;
- ~~74,55135~~ 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, Na₂SO₃ 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-% NH₃.

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.

Formatted: Font: 11 pt

Formatted: Space After: 6 pt, Line spacing: Exactly 11 pt

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.