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

*Pâtes — Liqueur Kraft — Détermination de la concentration en ions
hydrosulfurés par titrage potentiométrique*

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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).

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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.

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:

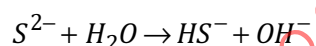
- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

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:



4 Principle

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



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



For white, green and black liquor, this document is applicable for hydrosulphide ion concentrations from 0,02 mol/litre to 2 mol/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/litre to 50 mmol/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 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 0,1 M, 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/litre to four decimal places.

Calculate the silver nitrate concentration, $[AgNO_3]$, in mol/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;

b is the amount of potassium chloride weighed, in milligrams;

74,551 3 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 1 M, dissolve 40,0 g of NaOH in 1,0 litre of oxygen-free water (5.1).

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

5.5 Ammonia, approximately 25 % NH_3 .

6 Apparatus

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

6.1 Automatic titration equipment, 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 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, 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 Pipette, volume 1 ml, 2 ml or 5 ml, calibrated.

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 lead 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 °C 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 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.

8.2 White, green and black liquors

Add approximately 40 ml of sodium hydroxide solution (5.3) and 5 ml ammonia (5.5) to the pre-treated sample. If the pretreatment has been omitted, increase the volume of sodium hydroxide solution to 50 ml.

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

8.3 Oxidized white liquors

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

If the pre-treatment has been omitted, increase the volume of sodium hydroxide solution to 70 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.

8.4 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 1 Two inflection points can be obtained in a pre-treated oxidized white and black liquor sample. The first inflection point at approx. -650 mV corresponds to hydrosulphide (HS^-) as described by reaction (1). The second inflection point at approx. -450 mV corresponds to methyl mercaptan (CH_3SH) as described by reaction (2). 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.

NOTE 2 Two inflection points obtained in the titration of a sample which has not been pre-treated means in most cases disturbance from polysulphide, see Figure 1. Neither of the inflection points in that case gives the correct hydrosulphide concentration.

NOTE 3 Sulphite does not interfere in the potentiometric titration. Due to the high pH-level, chloride does not disturb the titration either.

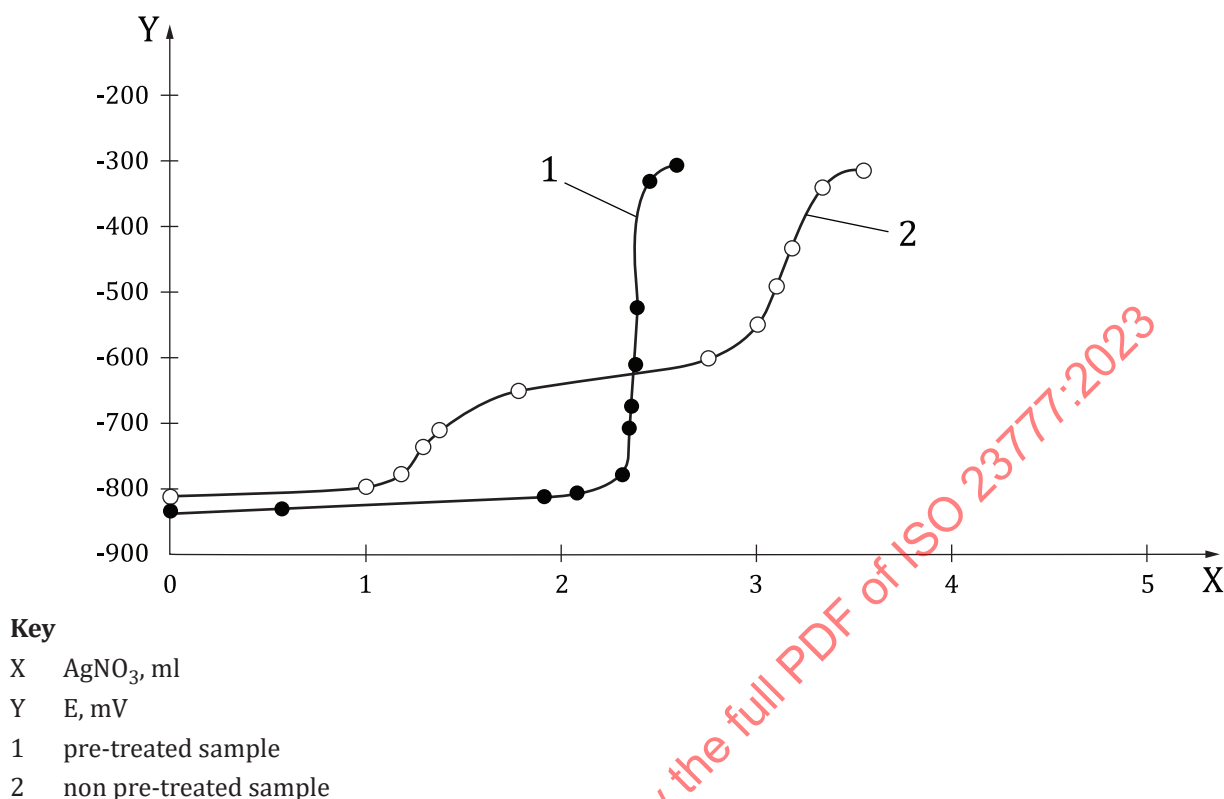


Figure 1 — Titration curves for pre-treated sample and non-pre-treated sample

If the non-pre-treated sample gives two inflection points, the result shall be rejected and pre-treatment shall be done before a new titration is carried out.

9 Calculation

9.1 Calculate the HS⁻ concentration in moles per litre according to [Formula \(6\)](#):

$$X_1 = \frac{C \cdot a}{2V} \quad (6)$$

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 two decimal places.

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

$$X_2 = 32X_1$$

where

X_2 is the HS^- content of the sample, in grams of sulphur per litre;

32 is the relative atomic mass of sulphur.

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

10 Report

The test report shall include the following:

- a) a reference to this document, i.e. ISO 23777:2023;
- b) date and place of testing;
- c) precise identification of the sample;
- d) if relevant, a statement that the pre-treatment has been omitted;
- e) if relevant, a statement that the -650 mV cell potential has been used to identify the endpoint of the titration;
- f) the result given to two significant figures;
- g) any departure from the standard procedure and any other circumstances that may have affected the result.

Annex A (informative)

Precision data

Three black liquors, a white liquor and a green liquor were included in the inter-laboratory study to develop this precision statement.

In [Table 1](#), the repeatability and reproducibility are presented as one standard deviation.

Table 1 — Repeatability and reproducibility as standard deviations

Hydrosulphide ion	Level Average mol/l	Repeatability (s_r) Standard deviation mol/l	Reproducibility (s_R) Standard deviation mol/l
Black liquor 1	0,21	0,000 53	0,006 5
Black liquor 2	0,037	0,000 35	0,003 8
Black liquor 3	0,30	0,000 85	0,016
White liquor	0,76	0,001 1	0,012
Green liquor	0,85	0,002 1	0,077

The difference between four test results found on identical test material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit (r), see [Table 2](#), on average not more than once in 20 cases in the normal and correct operation of the method.

Test results on identical test material reported by seven laboratories will differ by more than the reproducibility limit (R), see [Table 2](#), on average not more than once in 20 cases in the normal and correct operation of the method.

Table 2 — Repeatability and reproducibility, difference between two tests at 95 % probability level

Hydrosulphide ion	Level Average mol/l	Repeatability (r) Limit mol/l	Reproducibility (R) Limit mol/l
Black liquor 1	0,21	0,001 5	0,018
Black liquor 2	0,037	0,001 0	0,011
Black liquor 3	0,30	0,002 4	0,045
White liquor	0,76	0,003 1	0,034
Green liquor	0,85	0,005 7	0,21

The accuracy data were determined from an experiment organized and analysed in accordance with ISO 5725-2 in 2021 involving seven laboratories.

The repeatability and reproducibility are valid for liquids similar to the liquids evaluated for the precision statement. Other types of liquids, with properties different from the evaluated liquids, may have repeatability and reproducibility that are different from what is reported in this precision statement.

NOTE Not all laboratories homogenized the samples before analysing.