

DRAFT INTERNATIONAL STANDARD

ISO/DIS 23772

ISO/TC 6

Secretariat: SCC

Voting begins on:
2022-05-04

Voting terminates on:
2022-07-27

Pulps — Kraft liquor — Residual alkali (Hydroxide ion content)

ICS: 85.040

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23772

<https://standards.iteh.ai/catalog/standards/sist/54ffa698-f109-4755-9555-89594f0f8a73/iso-23772>

THIS DOCUMENT IS A DRAFT CIRCULATED FOR COMMENT AND APPROVAL. IT IS THEREFORE SUBJECT TO CHANGE AND MAY NOT BE REFERRED TO AS AN INTERNATIONAL STANDARD UNTIL PUBLISHED AS SUCH.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

This document is circulated as received from the committee secretariat.



Reference number
ISO/DIS 23772:2022(E)

© ISO 2022

iTeh STANDARD PREVIEW (standards.iteh.ai)

ISO 23772

<https://standards.iteh.ai/catalog/standards/sist/54ffa698-f109-4755-9555-89594f0f8a73/iso-23772>



COPYRIGHT PROTECTED DOCUMENT

© 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
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

| | |
|---|-----------|
| Foreword | iv |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Terms and definitions | 1 |
| 4 Principle | 1 |
| 5 Reagents | 2 |
| 5.1 General..... | 2 |
| 5.2 Sodium carbonate solution 1 M..... | 2 |
| 5.3 Hydrochloric acid 1 M..... | 2 |
| 5.4 Sodium hydroxide solution 1 M..... | 2 |
| 5.5 Ethanol..... | 2 |
| 5.6 Buffer solutions..... | 2 |
| 6 Apparatus | 2 |
| 6.1 General..... | 2 |
| 6.2 Automatic titrator or pH-meter..... | 3 |
| 6.3 Electrodes..... | 3 |
| 6.4 Fume hood..... | 3 |
| 7 Sampling and sample pretreatment | 3 |
| 8 Calibration and check of pH meter | 3 |
| 9 Procedure | 3 |
| 10 Calculation | 4 |
| 11 Report | 5 |
| Annex A (informative) Precision data | 6 |
| Bibliography | 7 |

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 is the first edition of the standard and it 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 — Residual alkali (Hydroxide ion content)

1 Scope

This standard describes a procedure for determining the content of residual alkali in Kraft black liquors having a dry matter content up to 40 %.

NOTE If the dry matter content of the sample exceeds 40 %, the sample needs to be diluted with distilled water to a dry matter content around 20 %.

The method is based on a potentiometric titration with hydrochloric acid and is intended for black liquor samples with an initial pH $\geq 11,0$.

The lower limit of determination is 0,1 g/l of eq. NaOH.

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 terminological 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

residual alkali

content of hydroxide ions remaining in the black liquor

Note 1 to entry: The hydroxide ions can result when sodium (or potassium) sulphide is dissolved in water and sulphide ions are hydrolysed.

Note 2 to entry: The result is expressed in moles of hydroxide ions per litre of sample or in grams of sodium hydroxide per litre of sample.

Note 3 to entry: Residual alkali is also known as residual effective alkali.

4 Principle

The alkaline species contained in the black liquor sample are titrated potentiometrically with hydrochloric acid to the first inflection point, which occurs at pH between 11,0 and 11,5. Before the titration, sodium carbonate is added to the sample to give a better inflection point and to buffer the titration solution. If the initial pH of the black liquor sample is between 11,0 and 12,5 a known volume of sodium hydroxide shall be added to the sample before the titration. The content of residual alkali is calculated from the consumption of the acid at the first inflection point. The result is corrected by a correction factor to obtain only the hydroxide ions concentration and remove the contribution of other alkaline species.

Precision data are available in [Annex A](#).

5 Reagents

5.1 General

All chemicals shall be of analytical grade. The water used in the titration and in the preparation of reagents shall be distilled or deionized.

WARNING — The use of this document can involve hazardous materials, operations and equipment. It does not purport to address all of the safety or environmental problems associated with its use.

5.2 Sodium carbonate solution 1 M

Dissolve 106,0 g of sodium carbonate, Na_2CO_3 in water and dilute to 1 litre with water.

5.3 Hydrochloric acid 1 M

The actual concentration of hydrochloric acid, HCl, shall be known to the nearest 0,001 M.

NOTE Commercially available standard solutions may be used.

5.4 Sodium hydroxide solution 1 M

Dissolve 40,0 g of sodium hydroxide, NaOH, in water in a 1 litre volumetric flask and dilute to the mark with water. Check the concentration by titration with a standard acid. The actual concentration shall be known to the nearest 0,005 M.

NOTE Commercially available standard solutions may be used.

5.5 Ethanol

Ethanol for washing the electrodes.

ISO 23772

<https://standards.iteh.ai/catalog/standards/sist/54ffa698-f109-4755-9555-89594f0f8a73/iso-23772>

5.6 Buffer solutions

Buffer solutions having pH values such as 7,0 and 11,0. Suitable buffer solutions are commercially available or can be prepared as follows:

pH 7,00, 25 °C:

Dissolve 6,80 g of potassium dihydrogen phosphate, KH_2PO_4 , previously dried for 2 hours at 105 °C, and 1,16 g of sodium hydroxide, NaOH, in water in a 1 litre volumetric flask and dilute to the mark.

pH 11,00, 25 °C:

Dissolve 3,55 g of disodium hydrogen phosphate, Na_2HPO_4 , previously dried for 2 hours at 105 °C, and 0,16 g of sodium hydroxide, NaOH, in water in a 1 litre volumetric flask and dilute to the mark.

6 Apparatus

6.1 General

Ordinary laboratory equipment.

6.2 Automatic titrator or pH-meter

An automatic device for potentiometric titration including a motorized burette (10 or 20 ml) and a recorder are recommended.

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

6.3 Electrodes

Suitable glass and reference electrodes. A combined pH glass electrode may be used.

NOTE 1 A high sodium pH-electrode is recommended.

NOTE 2 Clean the electrodes with ethanol (5.5) if the response time deteriorates.

6.4 Fume hood

A fume hood shall be used to ventilate any gases.

7 Sampling and sample pretreatment

The sample bottles shall be kept completely filled with black liquor and tightly closed to prevent oxidation by air.

NOTE Black liquor is sensitive to oxidation by air.

8 Calibration and check of pH meter

Operate the pH meter in accordance with the manufacturer's instructions. Wash the electrodes (6.3) with distilled water; allow the distilled water to drain from the electrodes.

Fill the titration vessel with the first standard buffer solution (5.6), measure the temperature of the solution and immerse the electrodes.

The first buffer solution shall be chosen so that the pH value of the solution is in the same region as the electric zero point of the pH meter (usually pH = 7).

Adjust the pH-meter so that it indicates the known pH of the first buffer solution at the actual measuring temperature. A slow but continuous increase or decrease in the reading indicates faulty electrodes.

Wash the electrodes with water as before and immerse them in the second standard buffer solution (5.6). The temperature of the second buffer solution shall not deviate by more than two degrees from the temperature of the first buffer solution. Adjust the meter, in accordance with the manufacturer's instructions, so that it indicates the known pH of the second buffer solution.

9 Procedure

Ensure that the black liquor 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.

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.

NOTE The exact sample volume is determined by the level of residual alkali. Usually the sample volume is 10 – 20 ml.

Run the determination in duplicate. Operate the titration equipment (6.2) as instructed by the manufacturer. Wash the electrodes (6.3) with distilled water, allow the distilled water to drain from the electrodes and insert them in the black liquor sample. Stir with a magnetic stirrer and measure

the pH of the sample at least twice. The temperature of the sample shall not deviate by more than five degrees from the temperature of the buffer solutions.

WARNING — Hydrogen sulphide can be formed during the titration. Since hydrogen sulphide is a toxic gas, the titration shall be performed under a hood or other measures shall be taken to protect the operator.

If the pH is below 11,0 the sample contains no residual alkali.

If the pH is between 11,0 and 12,5 an addition method shall be used. Add approximately 5 ml NaOH-solution (5.4) to the nearest 0,01 ml to the titration vessel before titration and follow the procedure described below.

If the initial pH of the sample is above 12,5 add 80 ml of water, 10 ml of sodium carbonate solution (5.2) and 10 ml of black liquor in a suitable vessel for titration. The amount of liquor can be reduced or increased, if necessary depending on the amount hydrochloric acid consumed. In this case the amount of water and sodium carbonate solution shall be adjusted correspondingly.

Insert the electrodes in the solution and stir with a magnetic stirrer. Titrate with hydrochloric acid (5.3) past the first inflection point so that an S-shaped curve is obtained. If an automatic device is not used, read the potentiometric value after each addition and construct the titration curve by plotting each reading against the corresponding total volume of hydrochloric acid (5.3) added. Read the volume of hydrochloric acid at the inflection point (a). If there is no distinct inflection point, read the volume of hydrochloric acid at pH 11,5. This shall then be mentioned in the report.

10 Calculation

Calculate the residual alkali from the expressions:

$$X_1 = \frac{0,95(aC_1 - bC_2)}{V} - 0,012 \quad (1)$$

$$X_2 = 40X_1 \quad (2)$$

$$X_3 = 31X_1 \quad (3)$$

where

X_1 is the residual-alkali content of the black liquor expressed as OH-, in moles per litre;

0,95 is a correction factor;

a is the volume of the hydrochloric acid consumed at the first inflection point, in millilitres;

C_1 is the concentration of hydrochloric acid (5.2), moles per litre;

b is the volume of the sodium hydroxide (5.3) added before the titration (here 5 ml), in millilitres;

C_2 is the concentration of sodium hydroxide solution (5.3), in moles per litre;

V is the volume of the sample, in millilitres;

-0,012 is a correction factor;

X_2 is the residual-alkali content of the black liquor expressed as NaOH, in grams per litre;

40 is the relative molecular mass of NaOH, in grams per mole;

X_3 is the residual-alkali content of the black liquor expressed as Na_2O , in grams per litre;

31 is the relative molecular mass of Na_2O , in grams per mole.

NOTE 1 Residual alkali is usually expressed in equivalent NaOH (g/L) in Europe, whereas in North America is usually expressed in equivalent Na_2O (g/L)

NOTE 2 If the value of the residual alkali is negative, then the result is expressed as $< 0,1$ g/l NaOH . The negative value indicates the amount of hydrochloric ions needed to titrate weak acids present in the solution.

NOTE 3 The correction factor (0,95) and correction term (-0,012) are explained as follows:

The hydroxide ion content calculated at the first inflection point of the titration gives an overestimated value.

The difference between the measured and true values of the hydroxide ion concentration depends on the acid/base properties of the organic and inorganic substances present in the black liquor. When the titration is performed according to this document where the pH-value is between 11,0 and 11,5, parts of these other species are also titrated. This is not the case when a reference method is used for the determination of the hydroxide ion content, since for this method the pH-range used is $> 12,5$. Thus the measured value according to this document always has to be corrected in order to obtain the true value of the hydroxide ion content.

The correction factors of the residual alkali in Equation (4) are based on the report by Ulmgren et al [3] and presented in SCAN N33-94 [5]. The true value of hydroxide ions is calculated by an extrapolation method using data from a potentiometric titration of a sample of the black liquor. According to this reference method the correction equation for all types of black liquors is:

$$\text{True} [\text{OH}^-] = 0,95 * \text{measured value} - 0,48 \quad (4)$$

where

<https://standards.iteh.ai/catalog/standards/sist/54ffa698-f109-4755-9555-89594f0f8a73/iso-23772>
 $\text{True} [\text{OH}^-]$ and *measured value* are expressed in g/l NaOH .

Calculate the mean value of at least two duplicate determinations. The results of the duplicate determinations shall not deviate by more than 5 % from their mean.

NOTE 4 The method shows good correlation when compared by measuring the residual effective alkali by capillary electrophoresis [4].

11 Report

The test report shall include reference to this standard and the following particulars:

- date and place of testing;
- identification mark of the sample tested;
- the method of determination used and if relevant identify the pH-endpoint of the titration;
- the measured starting pH of the sample;
- the result given to two significant figures;
- any departure from the standard procedure and any other circumstances that may have affected the result.

Annex A (informative)

Precision data

Three black liquors 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

| Residual alkali | Level Average g/l NaOH | Repeatability (s_r) Standard deviation g/l NaOH | Reproducibility (s_R) Standard deviation g/l NaOH |
|-----------------|------------------------------|---|---|
| Black liquor 1 | 7,4 | 0,016 | 0,40 |
| Black liquor 2 | 1,2 | 0,023 | 0,30 |
| Black liquor 3 | 21 | 0,025 | 0,47 |

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

| Residual alkali | Level Average g/l NaOH | Repeatability (r) Limit g/l NaOH | Reproducibility (R) Limit g/l NaOH |
|-----------------|------------------------------|--|--|
| Black liquor 1 | 7,4 | 0,045 | 1,11 |
| Black liquor 2 | 1,2 | 0,065 | 0,84 |
| Black liquor 3 | 21 | 0,068 | 1,31 |

The accuracy data were determined from an experiment organized and analysed in accordance with ISO 5725-2[6] in 2021 involving 7 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 analyzing.