ISO/FDIS 23774:2022(E)
ISO TC 6/WG 17
Date: 2022-~~10-17~~11-24

Pulps — Kraft liquor — Determination of total, active and effective alkali using potentiometric titration

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

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~~www.iso.org

Published in Switzerland

Contents

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.

Proposed title: Pulps — Kraft liquor — Determination of total, active and effective alkali using potentiometric titration

1 Scope

This document specifies a potentiometric titration procedure for the determination of total, active and effective alkali in white and green liquors obtained and used in the kraft or sulphate pulping process.

This document is not applicable for the analysis of liquors such as oxidized white liquors which contain significant amounts of polysulphides. The method given in this document is not intended for the determination of particular ionic species, such as sulphides or carbonates.

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
total alkali
total concentration of alkaline constituents determined by titration of a sample of the liquor with strong acid to the third inflection point according to specific requirements

Note 1 to entry: The specific requirements are described in this document, ISO 23774~~:xxxx, clause~~ ~~;~~—, Clauses 8 and 9

Note 2 to entry: See also Annex B.

3.2
active alkali
total concentration of alkaline constituents, except carbonates, as determined by titration of a sample of the liquor with strong acid according to specific requirements

Note 1 to entry: The specific requirements are described in this document, ISO 23774~~:xxxx, clause;~~—, Clauses 8 and 9

Note 2 to entry: In practice, active alkali is considered to be the sum of the concentrations of hydroxyl and hydrosulphide ions, including hydroxyl ions formed by hydrolysis of sulphides. See also Annex B.

3.3

effective alkali
concentration of strongly alkaline constituents determined by titration of a sample of the liquor with strong acid to the first inflection point according to specific requirements

Note 1 to entry: The specific requirements are described in this document, ISO 23774~~:xxxx, clause~~:—, Clauses 8 and 9

Note 2 to entry: In practice, this is considered to be the concentration of hydroxyl ions, including those formed from sulphides by hydrolysis. See also Annex B.

4 Principle

The determination of total, active and effective alkali in a liquor sample is based on an acidic dosage by a strong acid of the alkaline species contained in the sample. The major alkaline species in green liquor are hydroxyl ions (OH^-), hydrosulphur ions (HS^-), carbonate (CO_3^{2-}) and hydrogenocarbonate ions (HCO_3^-), whereas in white liquor they are mainly hydroxyl ions (OH^-) and hydrosulphur ions (HS^-). During the acidic dosage, these alkaline species lead to different inflexion points for specific pH ranges as described in Clause 8.

Field Code Changed

Field Code Changed

A sample of the liquor is titrated with hydrochloric acid of known concentration. The pH value (or a suitable function of the pH value) of the reaction mixture and the volume of hydrochloric acid are recorded continuously and from the recorded data the consumption of acid at the inflection points is determined.

NOTE The titration is preferably performed using an automatic titration equipment.

From the amounts of acid required to reach the three inflection points, the effective, active and total alkali of the sample are calculated.

Precision data are available in Annex A.

5 Reagents

~~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.

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

~~5.1~~ 5.1 Hydrochloric acid 1 M

~~The~~, the actual concentration of hydrochloric acid, HCl, shall be known to the nearest 0,005 M.

~~5.2 Buffer solutions~~

5.2 **Buffer solutions** of known pH values near 4 and 9. Suitable buffer solutions are commercially available. They can also be prepared in the laboratory as follows:

— **Buffer solution, pH 4,01**:
In a 1 000 ml volumetric flask dissolve 10,12 g of potassium hydrogen phthalate, $KHC_8H_4O_4$, in

water and dilute to the mark. There is normally no need to dry the salt. The solution is stable for 2 months.

— **Buffer solution, pH 9,18**:

In a 1 000 ml volumetric flask dissolve 3,80 g of sodium tetraborate decahydrate (borax), $Na_2B_4O_7 \cdot 10H_2O$, in water from which carbon dioxide has been expelled by boiling. Dilute to the mark. The solution is stable for 6 weeks. The solution will absorb carbon dioxide when in contact with ambient air. Therefore, keep the solution in a stoppered bottle and do not leave the bottle open more than absolutely necessary.

6 Apparatus

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

6.1 **Automatic titration equipment**, including glass and reference electrodes, that records the titration curve (pH against titrant consumed) or any function of the titration curve, such as the first derivative, so that the inflection points of the titration curve can be determined. A combined pH glass electrode may be used. Check the precision of the equipment as instructed in ~~clause~~Clause 7.

For the analysis of green liquors, titration equipment that automatically evaluates the inflection points shall be used.

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

7 Calibration and check of pH meter

Operate the pH meter in accordance with the manufacturer's instructions. Wash the glass and reference electrodes with water; allow the water to drain from the electrodes.

Fill a sample cup with the first buffer solution and immerse the electrodes. Adjust the meter so that it indicates the known pH of the buffer solution. If the reading slowly but continuously increases or decreases, this indicates faulty electrodes.

Wash the electrodes with water as before and immerse them in the second standard buffer solution. Do not readjust the meter. The reading shall now agree to within 0,2 pH unit with the value assigned to the buffer. Failure to do so indicates a faulty electrode.

8 Procedure

Operate the titration equipment as instructed by the manufacturer. Use ~~the~~ hydrochloric acid (5.1) as the titrant.

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

Choose the sample volume, v (ml), so that about half the burette capacity (or equivalent volume-measuring device) is used.

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.

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. Dilute the

sample with water to a suitable volume. Start the titration and note the volume of acid consumed as follows:

Volume consumed at the first inflection point:	a (ml)
Total volume consumed at the second inflection point:	b (ml)
Total volume consumed at the third inflection point:	c (ml)

NOTE Normally, the three inflection points appear at the following pH values:

1st inflection point - close to 11;

2nd inflection point- between 8 and 9;

3rd inflection point - close to 4.

9 Calculation

The results may be given in units of substance concentration (moles per litre) or in the conventional way as "grams of sodium hydroxide per litre" or "grams of sodium oxide per litre".

To obtain the results in moles per litre calculate according to formula (1) to (3):

~~$A_{eff} = \frac{a*m}{v}$~~ $A_{eff} = \frac{a*m}{v}$ (1)

~~$A_{act} = \frac{(2a-2b+c)m}{v}$~~ ~~(2)~~

~~$A_{tot} = \frac{c*m}{v}$~~ $A_{act} = \frac{(2a-2b+c)m}{v}$ (2)

$A_{tot} = \frac{c*m}{v}$ (3)

If the results are required in g NaOH per litre, multiply the above results by 40.

If the results are required in g Na_2O per litre, multiply the above results by 31.

~~Where~~

where

- A_{eff} is the effective alkali
- A_{act} is the active alkali
- A_{tot} is the total alkali
- m is the concentration of the hydrochloric acid in moles per litre;
- v is the volume of sample taken, in millilitres;
- a volume consumed at the ~~first~~ inflection point in ml;
- b total volume consumed at the second inflection point in ml;
- c total volume consumed at the third inflection point in ml;
- 40 is the relative molecular mass of NaOH, in grams per mole;
- 31 is the relative molecular mass of Na_2O, in grams per mole.

For calculation of sulphidity and degree of causticizing, see Annex B.