INTERNATIONAL STANDARD

**ISO 29681**

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# Paper, board and pulps — Determination of pH of salted water extracts

*Papier, carton et pâtes — Détermination du pH des extraits d'eau salée*

Reference number
ISO 29681:2009(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 29681 was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*.

# Introduction

It is well known that pulp fibres contain ionizable groups that are fixed to or present in the fibre wall. In order to fulfil the electro-neutrality, these groups are balanced by an equivalent number of positive charges, which can be either protons or various metal ions. Especially in pulp suspensions having a low ionic strength, this can give rise to a marked uneven distribution of mobile ions between the volume held by the fibre wall and the bulk suspension liquor. This means that the fibres act as an ion-exchanger. The ion-exchange can be modelled very well with the Donnan theory (References [3], [4] and [5]).

If a relatively clean fibre sample, e.g. fibres from a bleached chemical pulp of virgin fibres, is diluted in deionized water, the formed pulp suspension will have a very low ionic strength. In such a system, most of the cations present (including protons) will be concentrated in the water volume held by the fibre wall. If the pH is measured, it will be the pH of the bulk suspension liquor. By adding salt to the system during the soaking step in 8.1, the ion-exchange phenomena will be decreased so that the concentration of different cations will be the same in the water held by the fibre wall as in the bulk suspension liquor. Since process waters always contain a certain amount of ions, the measurement of pH after soaking in salted water will give a more realistic environment and thus more correct pH-values for clean pulp samples, i.e. samples with a low ionic strength.

It is necessary to be aware that the results will not be the same for pulps having a low ionic strength when measuring pH according to ISO 6588-1[1] or ISO 6588-2[2] and to this International Standard.

# Paper, board and pulps — Determination of pH of salted water extracts

## 1 Scope

This International Standard specifies a method for the determination of the pH of an aqueous extract of paper, board and pulps, in which the soaking and the measuring are performed in salted water (0,1 M KCl solution).

This International Standard is applicable to all kinds of paper, board and pulps, but is specifically applicable to bleached pulps from virgin fibres and to pulp samples having a low ionic strength for which the pH-value using this International Standard will give more realistic results related to mill conditions than those obtained with ISO 6588-1 or ISO 6588-2.

When deionized water is used and the sample has a low ionic strength, the suspension will have a very low ionic strength and the pH-value obtained in the measurement will not be that of the sample but that of the distilled water. When salted water is used in the soaking, there will be no concentration difference between the fibre wall and the surrounding water, and the pH-value measured will be that of the sample (in the fibre wall).

The use of salted water when dealing with samples having a low ionic strength also promotes more stable and more accurate pH-readings.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 186, *Paper and board — Sampling to determine average quality*

ISO 7213, *Pulps — Sampling for testing*

## 3 Terms and definitions

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

**3.1**
**salted water**
weak potassium chloride (KCl) solution, prepared as described in 5.3

## 4 Principle

The sample is soaked in salted water (0,100 M KCl) for 1 h. Soaking can be performed either at a temperature between 20 °C and 25 °C or at 90 °C. The suspension is filtered through a filter and the pH is measured at a temperature between 20 °C and 25 °C.

## 5 Reagents

**5.1 Distilled or deionized water**. The water shall be in equilibrium with atmospheric carbon dioxide, i.e. it should have a pH-value of between 5,6 and 6,2.

**5.2 Standard buffer solutions**, with known pH-values of about 4, 7 and 9, commercially available, or as described in Annex A.

The buffer solutions should be chosen so that the pH-value of the sample is between the pH-values of the buffer solutions.

**5.3 Salted water**, i.e. potassium chloride solution, $c(\mathrm{KCl}) = 0{,}100$ M. Weigh 7,45 g of reagent grade potassium chloride, KCl, and dilute with water (5.1) to 1 000 ml.

## 6 Apparatus and equipment

**6.1 pH-meter**, fitted with a measurement electrode and reference electrode, or a combination electrode of such design and in such condition that the pH of the filtrate can be measured with an error of less than 0,05 pH-units.

**6.2 Glassware**, of chemically resistant glass, flasks with ground-glass joints, stoppers, beakers and fritted glass filters.

NOTE Low ash (< 0,01 %) filter paper can be used instead of a fritted glass filter.

All glassware shall be cleaned with an acid cleaning solution, without the use of soap or detergent, and shall be carefully rinsed with distilled or deionized water (5.1) and allowed to dry before use.

**6.3 Thermostat bath or heating plate**, capable of maintaining the temperature at 90 °C.

**6.4 Balance**, accurate to ±1 mg.

## 7 Sampling and preparation of sample

If the analysis is being made to evaluate a lot of paper, board or pulp, take the sample in accordance with ISO 186 or ISO 7213, as relevant. If the analysis is made on another type of sample, report the origin of the sample and, if possible, the sampling procedure. Make sure that the test portion taken for analysis is representative of the sample received.

Never touch the sample with bare hands; use protective gloves. Cut the test portion into smaller pieces, e.g. with a size of 1 $\mathrm{cm}^2$ or less. Split pieces having a thickness exceeding 0,3 mm into thinner pieces.

Mix the test pieces of the test portion and store the test portion in a covered container.

## 8 Procedure

### 8.1 Soaking in salted water

Run the whole procedure in duplicate.

Air-dry the specimen in the laboratory atmosphere until it reaches moisture equilibrium.

Weigh between 2,0 g and 2,2 g of the air-dry test portion in a flask (6.2). Add 100 ml of salted water (5.3) having a temperature between 20 °C and 25 °C. Make sure that all the pieces are completely wetted. Close the flask and let it stand for 1 h, but shake the flask at least once during the standing time. Filter the suspension through a filter (6.2) before measurement. If it is required to soak at 90 °C, place the same weighed amount of sample in the flask and add 100 ml of salted water (5.3) having a temperature of (90 ± 5) °C. Place the flask in a thermostatic bath or on a heating plate (6.3) to keep the temperature at (90 ± 5) °C for 1 h. Shake the flask at least once during the heating time. Cool the suspension when the soaking is over and filter the suspension through a filter (6.2) before measurement.

### 8.2 Calibration of the pH-electrodes

Calibrate the pH-meter and the pH-electrodes (6.1) according to the manufacturer's instructions. If no such instructions are available, proceed as follows.

Wash the electrodes with water (5.1) and let them drain. Do not wipe them. Calibrate the pH-meter at a temperature between 20 °C and 25 °C with two different buffer solutions (5.2) having pH-values such that the pH of the extract is between the pH-values of the two buffer solutions. If the pH-meter fails to show the correct pH-value for the second buffer solution, consult the manufacturer's manual.

When they are not in use, store the electrodes as recommended by the manufacturer.

### 8.3 Measurement

After calibration according to 8.2, rinse the electrodes several times with water (5.1) and once with a small quantity of the filtered suspension, i.e. the extract. At a temperature between 20 °C and 25 °C, measure and record the pH of the duplicate extracts.

## 9 Calculation

Calculate the mean of the duplicate determinations. Report the pH of the sample to the nearest 0,1 pH-unit. The individual results shall not differ by more than 0,2 pH-units. If they do, repeat the determination with two new duplicates.

## 10 Precision

### 10.1 Repeatability

The pH-values of five different samples were determined in one laboratory according to this International Standard. Ten parallel determinations were made in each case. Mean values, standard deviations ($\sigma$), coefficients of variation (CV, %) and repeatability limits ($r$) for each type of sample are shown in Tables 1 and 2.

**Table 1 — Repeatability of salted cold water extract**

| Sample | pH | $\sigma$ | CV, % | $r$ |
|---|---|---|---|---|
| Bleached hardwood | 4,0 | 0,023 | 0,57 | 0,06 |
| Bleached softwood | 4,2 | 0,019 | 0,46 | 0,05 |
| Copy paper | 9,7 | 0,037 | 0,38 | 0,10 |
| Newspaper | 7,8 | 0,039 | 0,50 | 0,11 |
| Board | 7,6 | 0,029 | 0,38 | 0,08 |

**Table 2 — Repeatability of salted hot water extract**

| Sample | pH | $\sigma$ | CV, % | $r$ |
|---|---|---|---|---|
| Bleached hardwood | 3,9 | 0,019 | 0,49 | 0,05 |
| Bleached softwood | 4,1 | 0,020 | 0,48 | 0,06 |
| Copy paper | 9,3 | 0,055 | 0,59 | 0,15 |
| Newspaper | 7,5 | 0,033 | 0,45 | 0,09 |
| Board | 8,5 | 0,031 | 0,37 | 0,09 |

## 10.2 Reproducibility

The pH-values of five different samples were determined in six different laboratories according to this International Standard. Mean values, standard deviations ($\sigma$), coefficients of variation (CV, %) and reproducibility limits ($R$) for each type of sample are shown in Tables 3 and 4.

**Table 3 — Reproducibility of salted cold water extract**

| Sample | pH | $\sigma$ | CV, % | $R$ |
|---|---|---|---|---|
| Bleached hardwood | 3,7 | 0,205 | 5,5 | 0,57 |
| Bleached softwood | 4,0 | 0,204 | 5,1 | 0,57 |
| Copy paper | 9,7 | 0,395 | 4,1 | 1,1 |
| Newspaper | 8,0 | 0,272 | 3,4 | 0,75 |
| Board | 7,9 | 0,550 | 7,0 | 1,5 |

**Table 4 — Reproducibility of salted hot water extract**

| Sample | pH | $\sigma$ | CV, % | $R$ |
|---|---|---|---|---|
| Bleached hardwood | 3,7 | 0,174 | 4,7 | 0,48 |
| Bleached softwood | 4,0 | 0,260 | 6,5 | 0,72 |
| Copy paper | 9,5 | 0,395 | 4,1 | 1,1 |
| Newspaper | 7,4 | 0,261 | 3,5 | 0,72 |
| Board | 8,3 | 0,127 | 1,5 | 0,35 |

## 10.3 Comparison of results obtained using ISO 6588-1 and ISO 6588-2

A comparison of the results obtained using this International Standard and ISO 6588-1 and ISO 6588-2 is given in Annex B.

## 11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) the date and place of testing;

c) all the information necessary for complete identification of the sample;

d) the soaking temperature, 20 °C to 25 °C or 90 °C;

e) the mean pH, expressed as indicated in Clause 9;

f) any unusual features observed in the course of the test;

g) any departure from the procedure described in this International Standard, or any other circumstances which may have affected the result.

# Annex A
(informative)

# Preparation of standard buffer solutions

## A.1 General

All the reagents used shall be of recognized reagent grade. The buffer solutions shall be renewed at least once a month. The anhydrous salts in A.2 and A.3 shall be dried at 120 °C.

## A.2 Buffer solution of pH 4,0

**Potassium hydrogen phthalate**, 0,05 mol/l solution. Dissolve 10,21 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water (5.1) in a 1 litre volumetric flask and dilute to the mark.

The pH-value of this solution is 4,00 at 20 °C and 4,01 at 25 °C.

## A.3 Buffer solution of pH 6,9

**Potassium dihydrogen phosphate and disodium hydrogen phosphate solution**. Dissolve 3,39 g of potassium dihydrogen phosphate ($KH_2PO_4$) and 3,54 g of disodium hydrogen phosphate ($Na_2HPO_4$) in water (5.1) in a 1 litre volumetric flask and dilute to the mark.

The pH-value of this solution is 6,87 at 20 °C and 6,86 at 25 °C.

## A.4 Buffer solution of pH 9,2

**Disodium tetraborate solution**. Dissolve 3,80 g of disodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in water (5.1) in a 1 litre volumetric flask and dilute to the mark.

The pH-value of this solution is 9,23 at 20 °C and 9,18 at 25 °C.