
**Pulp, paper and board —
Determination of total chlorine and
organically bound chlorine**

*Pâtes, papier et carton — Dosage du chlore total et du chlore lié aux
matières organiques*

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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).

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

For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 11480:1997), which has been technically revised to include the option of using the Schöniger combustion method combined with ion chromatography.

Introduction

This document specifies two procedures for the determination of total and organically bound chlorine in pulp, paper and board. The microcoulometric method ([Clause 4](#)) is based on combustion in a heated tube followed by microcoulometric titration. The Schöniger method ([Clause 5](#)) is based on the so-called Schöniger combustion followed by ion chromatography.

The choice of procedure depends on the availability of the apparatus and on the risk of interference by bromine compounds in the sample. In the microcoulometric method, the result does not strictly represent the chlorine content since it includes part of any bromine present in the sample. This procedure should thus be avoided if there is a risk that the sample has a high bromine content.

More work is involved in the Schöniger method than in the microcoulometric method. However, since the end determination is performed by ion chromatography, the result is unambiguously chlorine. The Schöniger method also requires a larger sample. Consequently, the result is more representative. On the other hand, the microcoulometric method is faster and several replicate determinations can be performed in a short time.

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Pulp, paper and board — Determination of total chlorine and organically bound chlorine

1 Scope

This document specifies two alternative procedures for the determination of total and organically bound chlorine in pulp, paper and board. It is applicable to all types of pulp, paper and board. The lower limit of the determination is about 20 mg/kg.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 287, *Paper and board — Determination of moisture content of a lot — Oven-drying method*

ISO 638, *Paper, board and pulps — Determination of dry matter content — Oven-drying method*

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 <http://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.1

total chlorine

total amount of the element chlorine present

3.2

organically bound chlorine

amount of organically bound chlorine present

4 Microcoulometric method

4.1 Principle

Determination of the chlorine content of the sample by combustion under controlled conditions in a quartz tube at high temperature. The combustion gases are fed through an electrolyte solution where all chlorine, now transformed to hydrogen chloride, is absorbed and determined by microcoulometry. For determination of the organically bound chlorine content, the inorganic chlorine compounds are extracted with dilute nitric acid before combustion.

NOTE 1 If determination of organically bound chlorine is not required, the extraction with acid nitrate is omitted.

NOTE 2 Any bromine present will interfere and cause a positive error. For details, see 4.11.

4.2 Chemicals and reagents

All chemicals used shall be of analytical reagent grade. Water for the preparation of solutions, or used in the procedure, shall be distilled water of high purity or equivalent. High blanks (see 4.8) can be due to impure water. The water can then be purified by treating it with activated carbon (4.2.4).

4.2.1 Acid nitrate solution, stock solution. Dissolve 17 g of sodium nitrate (NaNO_3) in distilled water. Add 1,4 ml of nitric acid (HNO_3) density 1,40 g/ml, and dilute to 1 l with distilled water. (This solution is only required for the determination of organically bound chlorine.)

4.2.2 Acid nitrate solution, working solution. Dilute 50 ml of the stock solution (4.2.1) to 1 l with distilled water. (This solution is only required for the determination of organically bound chlorine.)

4.2.3 Sulfuric acid (H_2SO_4), density 1,84 g/ml.

4.2.4 Activated carbon, for adsorption of water-soluble organic material in the determination of organically bound chlorine. (Suitable carbon is provided by manufacturers of combustion apparatus.)

4.2.5 Electrolyte solution, for use in the microcoulometer. Dilute 75 ml of glacial (98 %) acetic acid (CH_3COOH) to 100 ml with water.

Addition of sodium perchlorate (NaClO_4) and sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) to the absorption solution is recommended by some manufacturers of microcoulometers. Such additions are optional.

One manufacturer recommends a solution prepared by dissolving 1,35 g of sodium acetate (NaCH_3COO) in 850 ml of glacial acetic acid and diluting to 1 000 ml with water.

4.2.6 Hydrochloric acid, $c(\text{HCl}) = 0,010\ 0\ \text{mol/l}$

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4.2.7 2-Chlorobenzoic acid reference solution. Dissolve 110,3 mg of $\text{ClC}_6\text{H}_4\text{COOH}$ in distilled water and dilute to 100 ml in a volumetric flask. This solution contains 250 mg of organically bound chlorine per litre. Dilute the solution as required before use.

4.2.8 Compressed gases. Oxygen is required for the combustion. Other gases may also be required in order to control the combustion. It is essential that all gases used are free from chlorine and bromine in any form.

NOTE It has been reported that chlorinated solvents have been used to clean the gas containers.

4.3 Precautions

Chlorine compounds in small quantities are present almost everywhere, in chemicals, on the surfaces of the equipment, on the skin and in the laboratory air. It is therefore of utmost importance to take every measure to avoid contamination of samples and solutions. In particular, the risk of contamination from the laboratory air should be observed. Such contamination can come from reagents (solvents) stored in the laboratory, as well as from outdoor sources, for example, a bleaching plant.

Clean all equipment before use with dilute nitric acid and flush with pure water.

4.4 Apparatus

Of the items listed below, items 4.4.1 through 4.4.4 are required only if organic chlorine has to be determined. Item 4.4.7 is required only if total chlorine has to be determined.

4.4.1 Conical flasks, 250 ml, of chemically resistant glass, with standard tapered glass stoppers or polytetrafluoroethylene (PTFE)-lined screw caps.

4.4.2 Shaker for the flasks (4.4.1), giving their contents a circular motion. Its power shall be adjustable so that the contents are kept in motion without reaching the stopper.

4.4.3 Filtering device, for vacuum filtration on filters of diameter about 25 mm.

4.4.4 Filters, polycarbonate, nominal pore width 0,4 µm, diameter to fit the filtering device (4.4.3) and having a maximum chlorine content of 0,5 µg.

Alternatively, specially designed filtering cups of heat-resistant glass or ceramic material may be used.

If high blank values (4.8) are obtained, the reason could be contaminated filters. They should be washed before use with stock solution (4.2.1) and then with water.

4.4.5 Combustion apparatus, consisting of a quartz tube connected to a cell for microcoulometric titration (4.4.6). A multizone furnace can heat the middle section of the tube to at least 950 °C and preferably 1 000 °C. A boat of quartz or other heat-resistant material fits into the tube. The boat can be moved from the cold end of the tube to its hot section. The tube shall be wide enough to accommodate a boat loaded with a filter (4.4.4). The apparatus has an oxygen supply and some means for maintaining a constant flow of oxygen through the tube. The oxygen stream may be diluted with an inert gas, such as argon or nitrogen. The combustion gases are fed through the microcoulometric cell for continuous titration of chloride ions.

If required, a heated washing device containing sulfuric acid (4.2.3) for cleaning and drying the gas stream may be inserted between the outlet of the combustion tube and the cell.

4.4.6 Microcoulometer, enabling the determination of 2 µg of chloride ion with a coefficient of variation of less than 10 %, calculated from repeated determinations of chloride ion.

4.4.7 Sample cups, capacity about 1 ml, of quartz or other heat-resistant material, designed to fit into the sample boat. The use of these cups is optional.

4.5 Pretreatment of the sample

Keep samples protected from ambient air in polyethylene bags or in packages of aluminium foil. Use protective gloves whenever handling the sample. Check that no chlorine-containing material is transferred from the gloves to the sample.

Air-dry wet pulp at a temperature not exceeding 40 °C. Using a separate sample, determine the dry matter content as described in ISO 638 or ISO 287, as relevant.

Tear or cut the sample into small pieces using tweezers or scissors. The size of the pieces shall be adapted to the nature of the sample, as well as to the dimensions of the combustion equipment.

Split samples of pulp or paperboard to ensure complete soaking of the sample during the extraction step. If the soaking is incomplete, the results for organically bound chlorine may be too high.

Grind samples of coated or multi-ply paper and paperboard in a small mill, Wiley type or similar. The mill shall not be used for other purposes in order to avoid contamination of samples. Clean the mill carefully after each use.

The total amount of sample required depends on its chlorine content and is limited by the dimensions of the combustion apparatus. Normally, the amount of sample required for each single determination is between 10 mg to 60 mg.

For the determination of both parameters, a total of four sample portions is required. Weigh each sample portion to the nearest 0,1 mg. All samples should have approximately the same mass.

Of the four samples, two are taken for determination of total chlorine, and two are extracted with acid nitrate solution.

NOTE If determination of organically bound chlorine is not required, proceed directly to 4.7.

4.6 Extraction with acid nitrate solution

Transfer the two duplicate samples to 250 ml conical flasks with glass stoppers. Add 100 ml of the acid nitrate solution (4.2.2) and 15 mg of activated carbon (4.2.4) to each flask. At the same time, start two blanks without any sample. Close the flasks and shake them vigorously to wet the sample entirely. Place the flasks in a mechanical shaking machine and shake them for at least 1 h.

When analysing coated or filled papers containing large amounts of carbonate pigments, check that the mixture in the flask is still acid. If not, acidify the mixture by adding more of the acid nitrate solution (4.2.2).

Using the filtering device (4.4.3), filter the contents of the flasks on a polycarbonate filter or in a filtering cup (4.4.4).

Rinse the flask and the sides of the filtering funnel with small portions of the acid nitrate solution (4.2.2), about 25 ml in all. Finally, wash with a small portion of water. Apply suction until excess liquid has been removed.

Drawing large volumes of air through the filter should be avoided, as this can lead to contamination from halogen compounds present in the ambient atmosphere. On the other hand, any excess washing solution present in the filter can result in condensation of water in the combustion tube. Condensed water in the tube can interfere with the combustion (4.7). If the filter is too dry, it can ignite in the drying zone of the oven, which can lead to a low result.

4.7 Combustion

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In principle, the procedure is the same for unextracted and extracted samples. In practice, the procedure has to be adapted to the condition of the sample. Extracted samples (for the determination of organically bound chlorine) are wet, and samples for the determination of total chlorine are normally dry.

Operate the combustion apparatus (4.4.5) as instructed by the manufacturer. Several makes of apparatus are on the market. They differ in details and the procedure to be followed has to be adapted to the type of apparatus used. (See Annex C.)

Check the performance of the microcoulometer (4.4.6) by adding known amounts of hydrochloric acid (4.2.6) to the cell. The results should be within 5 % of the theoretical value.

Check the instrument regularly by operating it as instructed for samples, but use no sample.

NOTE Memory effects (false readings are obtained with no sample, in particular after running a sample with a high chlorine content) can be due to corroded combustion tubes.

If the sample is a wet fibre pad on a polycarbonate filter, fold the filter with a pair of forceps and place it in the boat.

If the sample is dry, place it in a sample cup (4.4.7) and load the boat with this cup. The use of sample cups may not be possible with all types of apparatus. The procedure may be modified as required.

Move the boat with the sample to the drying zone of the furnace and allow the water to evaporate. The time required for this depends not only on the amount of water to be removed but also on the design of the apparatus. No water should condense in the cooler parts of the combustion tube.

It is essential that the combustion be controlled at a slow rate so that no soot or condensed water remains upstream of the furnace. If this is the case, take the necessary steps to move all soot and water downstream before taking any reading.

Move the boat to the hot section of the tube. Follow the course of the combustion on the recording device of the instrument. Ensure, by the procedures relevant to the instrument, that the combustion is complete.

If soot is detected downstream from the furnace, the combustion has been incomplete and the result shall be rejected.

There should be no soot in the sulfuric acid in the heated washing device (4.4.5). If soot is observed, clean the device, add fresh sulfuric acid and repeat the determination.

4.8 Blanks

On each day that samples are analysed, check the combustion apparatus (4.4.5) and the microcoulometer (4.4.6), by running at least two blanks by the same procedure as for the samples. The blank value should not exceed 2 µg.

4.9 Checks

Check the entire procedure regularly by running a reference sample of known chlorine content. The reference sample should preferably be of the same type (pulp, paper, board, etc.) as the samples to be analysed.

If no reference sample is available, the chlorine content of a selected sample should be determined by the method of standard additions, using known amounts of the chlorobenzoic acid reference solution (4.2.7). This sample should be used as the reference sample.

The result of the check run should not be less than 91 % or more than 110 % of the assigned value. If the value falls outside the limits given, run a second check. If the deviation persists, check the apparatus for leaks and other defects. Instructions for performing this check should be given in the operating manual.

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4.10 Calculation

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The procedure for determining the chlorine content of the samples depends on the design of the microcoulometer. See the manufacturer's manual for instructions.

In calculation, ensure that the blank value is allowed for and that a correction for the moisture content of the sample is made.

Calculate the mean result of parallel determinations. The individual results should not deviate from the mean by more than 10 % (see Annex A for additional information). For mean values less than 50 mg/kg, deviations of up to 5 mg/kg are acceptable. If this criterion is not met, the sample may be heterogeneous. In this case, repeat the preparation of sample and the determination.

Express the results as total chlorine or organically bound chlorine, as relevant, in milligrams per kilogram, with two significant figures.

4.11 Interference from bromine compounds

Chemically bromine will react in the same way as chlorine under the conditions prevailing during the analysis described in this document. This means that any bromine present in the sample will cause a positive error in the result. The magnitude of this error is proportional, but not equal, to the amount of bromine present. The coulometers used are programmed to measure chlorine. If bromine is to be determined, the coulometer has to be recalibrated since bromine has a much higher atomic mass than chlorine.

Normally, the amounts of bromine present in pulp and paper are negligible. Occasionally, significant amounts of bromine have been found in products of recycled fibre from waste paper containing brominated slimicides.