INTERNATIONAL STANDARD

ISO 11480

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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

Reference numbe
ISO 11480:1997(E)

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.

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.

International Standard ISO 11480 was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*.

Annex A of this International Standard is for information only.

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

1 Scope

This International Standard specifies 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 standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 186:1994, *Paper and board — Sampling to determine average quality*.

ISO 287:1985, *Paper and board — Determination of moisture content — Oven-drying method*.

ISO 638:1978, *Pulps — Determination of dry matter content*.

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 total chlorine: The total amount of the element chlorine present.

3.2 organically bound chlorine: The amount of organically bound chlorine present.

4 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.

NOTES

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

2 Any bromine present will interfere and cause a positive error. For details, see clause 16.

5 Chemicals and reagents

All chemicals used should 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 clause 11) can be due to impure water. The water can then be purified by treating it with activated carbon (5.4).

5.1 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 litre with distilled water. (This solution is only required for the determination of organically bound chlorine.)

5.2 Acid nitrate solution, working solution. Dilute 50 ml of the stock solution (5.1) to 1 litre with distilled water. (This solution is only required for the determination of organically bound chlorine.)

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

5.4 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.)

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

NOTE — Addition of sodium perchlorate ($NaClO_4$) and sulfamic acid (NH_2SO_3H) 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.

5.6 Hydrochloric acid, $c(HCl)$ = 0,010 0 mol/l.

5.7 2-Chlorobenzoic acid reference solution. Dissolve 110,3 mg of ClC_6H_4COOH 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.

5.8 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.

6 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. Especially, 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.

7 Apparatus

Of the items listed below, items 7.1 through 7.4 are required only if organic chlorine has to be determined. Item 7.7 is required only if total chlorine has to be determined.

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

7.2 Shaker for the flasks (7.1) giving their contents a circular motion. Its power shall be adjustable so that the contents are kept in motion without reaching the stopper.

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

7.4 Filters, polycarbonate, nominal pore width 0,4 µm, diameter to fit the filtering device (7.3) 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.

NOTE — If high blank values (11) are obtained, the reason may be contaminated filters. They should be washed before use with stock solution (5.1) and then with water.

7.5 Combustion apparatus, consisting of a quartz tube connected to a cell for microcoulometric titration (7.6). 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 (7.4). 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 (5.3) for cleaning and drying the gas stream may be inserted between the outlet of the combustion tube and the cell.

7.6 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.

7.7 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.

8 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 has to 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 must 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 and 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 clause 10.

9 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 (5.2) and 15 mg of activated carbon (5.4) 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 (5.2).

Using the filtering device (7.3), filter the contents of the flasks on a polycarbonate filter or in a filtering cup (7.4).

Rinse the flask and the sides of the filtering funnel with small portions of the acid nitrate solution (5.2), about 25 ml in all. Finally wash with a small portion of water. Apply suction until excess liquid has been removed.

NOTE — Drawing large volumes of air through the filter should be avoided, as this may lead to contamination from halogen compounds present in the ambient atmosphere. On the other hand, any excess washing solution present in the filter may result in condensation of water in the combustion tube. Condensed water in the tube may interfere with the combustion (clause 10). If the filter is too dry it may ignite in the drying zone of the oven, which might lead to a low result.

10 Combustion

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 (7.5) 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 A.)

Check the performance of the microcoulometer (7.6) by adding known amounts of hydrochloric acid (5.6) 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 1 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 (7.7) and load the boat with this cup.

NOTE 2 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 (7.5). If soot is observed, clean the device, add fresh sulfuric acid and repeat the determination.

11 Blanks

On each day that samples are analysed, check the combustion apparatus (7.5) and the microcoulometer (7.6), by running at least two blanks by the same procedure as for the samples. The blank value should not exceed 2 µg.

12 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.

NOTE — 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 (5.7). 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.

13 Calculation

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 %. 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.

Repeat the preparation of sample and the determination.

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

14 Precision

14.1 Repeatability

Repeated analysis (5 determinations) gave the following results.

Table 1

Mean value mg/kg	**Standard deviation** mg/kg	**Coefficient of variation** %
Total chlorine		
66	3,3	5
310	3,1	1
650	13	2
970	19	2
Organically bound chlorine		
17	0,6	3,7
31	1,5	4,9
120	3,7	3,1
290	7,3	2,5
1 600	89	5,6

14.2 Reproducibility

An interlaboratory study comprising 14 laboratories in 8 different countries gave the results shown in the table below. The laboratories were asked to analyse the samples in triplicate. The means and standard deviations given are based on the average values obtained in each laboratory.

Table 2

Sample No.	Number of labs	Mean value mg/kg	Standard deviation mg/kg
Total chlorine			
1	14	560	28,3
2	14	367	25,3
3	14	207	10,2
4	13	347	20,8
Organically bound chlorine			
1	14	224	25,3
2	14	339	27,1
3	14	193	18,5
4	11	26	10,3

The samples were:

1 Copier paper

2 ECF birch pulp

3 ECF pine pulp

4 Copier paper made from TCF pulp

ECF means “elemental chlorine-free pulp”.

TCF means “totally chlorine-free pulp”.

15 Test report

The test report shall include the following particulars:

a) reference to this International Standard;

b) date and place of testing;

c) complete identification of the sample tested;

d) mean of the results, expressed in milligrams per kilogram;

e) any departure from the standard procedure that may have affected the result.

16 Interference from bromine compounds

Chemically bromine will react in the same way as chlorine under the conditions prevailing during the analysis described in this International Standard. 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.

Annex A
(informative)

Laboratory manuals

The procedure applied in this International Standard relies upon instruments of considerable complexity. Several manufacturers have introduced such instruments into the world market. They are all based on the same principle, but differ in details.

It is a principle in standardization not to specify the use of equipment produced by a particular manufacturer. The reason for this is not only that a standardization body should be neutral in respect to the competition between companies, but also to avoid specifications that unnecessarily will prevent further development of equipment.

In practice, this means that the course of the analysis cannot be described in this International Standard in such detail that it can be used as a laboratory bench manual. For the performance of the analysis, a number of informational details have to be taken from the manufacturer's manual or be established locally in preliminary tests. Examples are settings of gas flows, temperatures, power, waiting times, etc.

In order to facilitate the bench work and to ensure that all details of the procedure applied at any time can be traced, it is essential that a detailed bench manual be prepared, taking into account both the requirements of this International Standard and the manufacturer's instructions. A logbook should also be kept for recording the date and reason for all changes of procedure.