



Pulps (dried market pulps)

AOX, COD and TOC removable by washing

0 Introduction

This SCAN-test Method replaces SCAN-CM 44:91 from which it differs in that the possibility of determining COD and TOC removable by washing has also been included.

Since the pretreatment of the sample is the same, i.e. only the end-determination procedures differ, all the determinations are included in one Method.

The procedures described are applicable to the determination of substances removable by washing from dried pulps. The Method can be used to estimate the amount of substances which may be a load on the environment of the paper mill when the purchased, dried pulp is slushed.

Note – SCAN-CM 45 Kraft pulps – Water soluble organic matter is applicable to wet kraft pulps and is intended for the estimation of the efficiency of a washing operation and for the measurement of the amount of water-soluble organic matter carried to a subsequent section of the mill or to the environment.

1 Scope

This SCAN-test Method describes the procedure for determining COD, AOX and TOC removable by washing from dried market pulp. The Method is applicable to all kinds of chemical and mechanical pulps.

Only references to national standards or ISO Standards are given for the end-determination procedures of AOX, COD and TOC. The lower limits of determination are as follows:

AOX:	5 g/tonne oven-dry pulp
COD, titrimetric procedure:	2 kg/tonne oven-dry pulp
COD, ampoule procedure:	1 kg/tonne oven-dry pulp
TOC:	1 kg/tonne oven-dry pulp

2 References

ISO 638	Pulps – Determination of dry matter content – Oven-drying method (EN 20638)
ISO 5263-1	Pulps – Laboratory wet disintegration – Part 1: Disintegration of chemical pulps (EN ISO 5263-1)

Note – SCAN-test has withdrawn a number of test methods and refers instead to the corresponding ISO and/or EN Standards.

For the AOX end-determination procedure:

EN 1485	Water quality – Determination of adsorbable organically bound halogens
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For the COD end-determination procedure:

ISO 6060	Water quality – Determination of the chemical oxygen demand
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or

SS 02 81 42	Determination of chemical oxygen demand in water – COD _{Cr} oxidation with dichromate
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SFS 5504	Determination of chemical oxygen demand (COD _{Cr}) in water with the closed tube method. Oxidation with dichromate
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or

NS 4748-2 Determination of chemical oxygen demand in water. Oxidation with dichromate (COD_{Cr})

For the TOC end-determination procedure:

ISO 8245 Water quality – Guidelines for the determination of total organic carbon (prEN 1484, SS 02 81 99 = ISO 8245, SFS ISO 8245, NS ISO 8245)

3 Definitions

For the purpose of this Method, the following definitions apply:

3.1 *Substance removable by washing* – The amount of substance, which is removed from dried market pulp by the standardized washing procedure described in this Method.

3.2 *Adsorbable organic halogens (AOX)* – The mass concentration of the elements chlorine, bromine and iodine that is bound in dissolved or suspended organic matter and that is determined under specified conditions.

The AOX value is regarded as the mass of organically bound chlorine, determined as specified, present in a volume of water.

3.3 *Chemical oxygen demand (COD)* – The mass concentration of oxygen, equivalent to the amount of dichromate consumed by dissolved and suspended matter when a sample is treated with that oxidant under defined conditions.

Note 1 – This definition is given in ISO 6060.

3.4 *Total organic carbon (TOC)* – The quantity of carbon present in water in that organic matter which is dissolved or suspended in the water.

Note 2 – This definition is given in ISO 8245.

4 Principles

The pulp sample is disintegrated in water under specified conditions. The suspension formed is filtered on a filter.

The AOX in the filtrate is determined by adsorption to active carbon, followed by combustion and coulometric titration of the hydrochloric acid formed.

The COD in the filtrate is determined from the reduced part of the dichromate by using a spectrophotometric procedure (ampoules) or by a titrimetric procedure.

The TOC in the filtrate is determined as CO_2 after oxidation of the organic matter. Different principles for the determination of the CO_2 can be used.

The COD, AOX and TOC removable by washing of the dried market pulp are calculated.

5 Reagents

5.1 *Distilled or deionized water* or water of equivalent purity. The quality of the water is important for the precision of the results. The quality of the water is checked by running a blank as described in 8.3.

5.2 *Reagents for the end-determination procedure*, depending on the procedure chosen, see relevant standard.

6 Apparatus

6.0 *Ordinary laboratory equipment*, and the items listed below:

Note – The equipment used in the determination shall be scrupulously clean and shall be protected from dust.

6.1 *Wet disintegrator*, as described in ISO 5263-1, irrespective of whether mechanical or chemical pulp is to be disintegrated.

6.2 *Filtration device*, consisting of a filtering flask, a funnel and a vacuum pump.

6.3 *Glass-fibre filter*, without any addition of binders, having a grammage between 50 g/m² and 100 g/m², circular with a diameter to fit the funnel (6.2).

7 Sampling and sample pre-treatment

Use protective gloves whenever handling the sample. The sampling procedure is not covered by this Method. Make sure that the test pieces taken to disintegration are representative of the sample received.

Determine the dry matter content of the sample as described in ISO 638.

If AOX removable by washing is to be determined, take care to minimize the exposure of the sample to air in order to protect it from any contamination by chlorine or chlorine compounds present in the environment.

8 Washing procedure

8.1 Disintegration

Run the whole procedure in duplicate.

If the pulp is in sheet form, tear the pulp into pieces (approximately 15 mm × 15 mm) before soaking. For mechanical pulp as well as chemical pulp, weigh approximately 30 g as oven-dry sample with an accuracy of 0,1 g. Transfer the sample to a beaker and add 2000 ml of water (5.1). For all types of pulps, soak for between 4 h and 5 h.

Transfer the wetted pulp and the water (2000 ml volume) to a disintegrator (6.1). Do not rinse the beaker with water. Disintegrate by making 30 000 revolutions using the equipment described in ISO 5263-1 irrespective of if the pulp is of chemical or mechanical character.

Make sure that the pulp is completely disintegrated (see instructions given in ISO 5263-1).

8.2 Filtration

Immediately after disintegration, filtrate the disintegrated pulp suspension using the filtration device (6.2), the glass-fibre filter (6.3) and vacuum. Transfer a suitable portion of the pulp suspension to the funnel. Reject the first part of the filtrate, then collect the filtrate and transfer it to a flask. To make sure that the filtrate is not diluted, do not wash the fibre pad formed. If the end-determination procedures are not performed on the same day, preserve the filtrate using a preservative or by freezing.

Warning – Fibres present in the filtrate will cause results that are too high. Make sure that no fibres appear in the filtrate after the filtration. If fibres appear, filter the filtrate once more through the fibre pad.

Note – Only the amount of pulp suspension needed to give a sufficient volume for the end-determination procedure intended (AOX, COD and/or TOC), need to be filtered.

8.3 Blank test

Run a blank through the whole procedure using the same water that is used in the disintegration procedure.

9 End-determination procedures

9.1 AOX determination

Run the end-determination procedure according to the standard method chosen (2).

9.2 COD determination

Run the end-determination procedure according to the standard method chosen (2).

9.3 TOC determination

Run the end-determination procedure according to the standard method chosen (2).

10 Calculation

10.1 AOX calculation

Calculate the AOX removable by washing of the pulp using the expression:

$$Y_1 = \frac{1000 \cdot V(X - X_0)}{m} \quad [1]$$

where

- Y_1 is the AOX removable by washing, in milligrams per kilogram oven-dry pulp;
- X is the AOX in the filtrate, in milligram per litre;
- X_0 is the AOX in the blank, in milligram per litre;
- V is the volume of the water used in the disintegration (normally 2,0 litres), in litre;
- m is the oven-dry mass of the pulp, in gram;

Calculate the mean of the duplicate determinations and report the result to the nearest whole number in milligram per kilogram oven-dry pulp.

10.2 COD and TOC calculations

Calculate the COD or TOC removable by washing of the pulp using the expression:

$$Y_2 = \frac{V \cdot (X - X_0)}{m} \quad [2]$$

where

- Y_2 is the COD or TOC removable by washing, in kilogram per tonne oven dry pulp;
- X is the mass concentration of COD or TOC in the filtrate, in milligrams per litre;
- X_0 is the mass concentration of COD or TOC in the blank, in milligrams per litre;
- V is the volume of the water used in the disintegration (normally 2,0 litres), in litre;
- m is the oven-dry mass of the pulp, in gram;

Calculate the mean of the duplicate determinations. Report results from the determination of COD and TOC in kilogram per tonne oven-dry pulp with two significant figures.

11 Report

The test report shall include a reference to this SCAN-test Method and the following particulars:

- (a) date and place of testing;
- (b) precise identification of the sample;
- (c) for the AOX, COD and TOC end-determination procedures, the standard method used;
- (d) the results;
- (e) any deviation from the procedure described in this Method or any other circumstances which may have affected the test results.

12 Precision

12.1 Repeatability

12.1.1 Determination of AOX

One laboratory analysed, according to SCAN-W 9 (nowadays replaced by EN 1485), AOX removable by washing ten times with the following results:

Pulp	AOX, mg/kg	
	mean	CV, % *
Softwood, ClO ₂ -bleached	6,4	5,3

* CV is the coefficient of variation calculated with respect to the mean value.

12.1.2 Determination of COD

Two laboratories analysed, one using the photometric procedure according to SFS 5504, and the other the titrimetric procedure according to ISO 6060, COD removable by washing several times with the following results:

Pulp	COD, kg /tonne, photometric procedure		COD, kg /tonne, titrimetric procedure	
	mean	CV, %	mean	CV, %
	Bl. sulphite	7,0	4,4	6,9
Bl. sulphate	1,9	6,7	-	-

The repeatability results are based on 10 individual disintegrations, and precision data are reported separately for the photometric procedure and the titration procedure.

12.1.3 Determination of TOC

One laboratory analysed, according to ISO 8245, TOC removable by washing ten times with the following results:

Pulp	TOC, kg/tonne	
	mean	CV, %
Softwood, ClO ₂ -bleached	1,0	5,7

12.2 Reproducibility

12.2.1 Determination of AOX,

Six laboratories analysed, according to SCAN-W 9 (nowadays replaced by EN 1485), AOX removable by washing in three different pulp samples with the following results:

Pulp	AOX, mg/kg	
	mean	CV, %
Hardwood, ClO ₂ -bleached	11,4	12,7
Softwood, ClO ₂ -bleached	< 5 (4,2)**	13,8
Softwood, Cl-bleached	40	16,0

** below the lower limit of determination

12.2.2 Determination of COD

Nine laboratories analysed COD removable by washing using the photometric procedure (Dr Lange Ampoules), and two laboratories analysed, according to ISO 6060, COD removable by washing using the titration procedure. The results were as follows:

Pulp	COD, kg/tonne photometric procedure		COD, kg/tonne titrimetric procedure	
	mean	CV, %	mean	CV, %
	Bl. sulphite	7,0	9,8	7,6
Bl. sulphate	2,3	11,3	2,5	7,8

The reproducibility results are based on the mean values of COD from duplicate determinations from one disintegration and precision data are reported separately for the photometric procedure and the titration procedure.

12.2.3 Determination of TOC,

Five laboratories analysed, according to ISO 8245, TOC removable by washing in three different pulp samples with the following results:

Pulp	TOC, kg/tonne	
	mean	CV, %
Hardwood ClO ₂ -bleached	< 1 (0,9)**	56,2
Softwood ClO ₂ -bleached	< 1 (0,7)**	31,7
Softwood Cl-bleached	2,5	12,8

** below the lower limit of determination

SCAN-test Methods are issued and recommended by KCL, PFI and STFI-Packforsk for the pulp, paper and board industries in Finland, Norway and Sweden. Distribution: Sekretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, SE-114 86 Stockholm, Sweden.