SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

SCAN-C 45:00
Revised 2000

Pulp (wet, never-dried chemical pulp)

COD and TOC removable by washing

0 Introduction

This SCAN-test Method replaces SCAN-CM 45:91 from which it differs in that the washing solution has been changed from 0,001 mol/l NaOH to water and that the possibility of determining TOC removable by washing has been included.

The reason for replacing NaOH by water is that the same washing solution can be used regardless of the pH of the pulp. In addition, the same washing solution is used in this method as in SCAN-CM 44 *Pulps (dried market pulps) – AOX, COD and TOC removable by washing.*

The Method is intended for the estimation of the efficiency of a washing operation on a washing filter, on a press washer or on a dewatering press and for the measurement of the amounts of COD and TOC carried to a subsequent section of the mill or to the environment. In some situations the COD balance is incorrect, i.e. the total COD in the outlet (washed pulp + filtrate) exceeds the total COD in the inlet (pulp in + wash liquor). This situation is described in Annex A.

> *Warning 1* – The pH and the ionic strength will highly influence the result, i.e. the amount of substances removable by washing. Thus, this method should not be used for comparisons of pulps having different pH-value.

The substances removable by washing, as described in this method, are considered not as the total amount of the substance but as the amount of substance present in the water phase surrounding the fibre (13.3).

Only references to national standards or ISO Standards are given for the end-determination procedures of COD and TOC.

> *Warning 2* – Any peroxide or chlorate residue in the pulp will disturb the COD result obtained. If peroxide or chlorate is present in the sample, check their residues and correct the COD value obtained. Procedures for correction of the COD-value, caused by disturbances from presence of peroxide residue have been published (13.1).

1 Scope

This SCAN-test Method describes a procedure for determining COD and TOC removable by washing from chemical pulps withdrawn from a production stage. It is applicable to wet, never-dried chemical pulps having a concentration exceeding 1,5 %.

The lower limits of determination are approx. as follows:

COD, titrimetric procedure:	5 kg/tonne oven-dry pulp
COD, ampoule procedure:	3 kg/tonne oven-dry pulp
TOC:	3 kg/tonne oven-dry pulp

> *Note* – The lower limit of determination in this method is higher than the limit in SCAN-CM 44. The reason is that a dilution of the filtrate is included in this method, which is not the case in SCAN-CM 44.

2 References

2.1 General

ISO 4119 Pulps – Determination of stock concentration (EN ISO 4119)

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.

2.2 For the COD end-determination

ISO 6060 Water quality – Determination of the chemical oxygen demand

or

SS 02 81 42 Determination of chemical oxygen demand in water – COD_{Cr} oxidation with dichromate

or

SFS 5504 Determination of chemical oxygen demand (COD_{Cr}) in water with the closed tube method. Oxidation with dichromate

or

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

2.3 For the TOC end-determination

ISO 8245 Water quality – Guidelines for the determination of total organic carbon and dissolved organic carbon

or

EN 1484 Water analysis – Guidelines for the determination of total organic carbon and dissolved organic carbon

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 wet pulp by the standardised washing procedure described in this Method.

3.2 *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 6060:1989.

3.3 *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 8245:1987.

4 Principle

To a sample of wet, never-dried, pulp, water is added to yield a pulp concentration of about 15 g/1. The slurry is disintegrated and an aliquot of the suspension is filtrated through a filter on a Büchner funnel. The pulp mat on the filter is washed with water. The COD and/or TOC of the filtrate are determined.

The results are expressed in kilograms per tonne pulp (calculated on an oven-dry basis).

5 Reagents and chemicals

5.1 *Distilled* or *deionized water* or water of equivalent purity.

Note – The quality of the water is important for the precision of the results. Running a blank, as described in 8.3, checks the quality of the water.

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

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

6.3 *Filter*, made from glass fibre or paper, with high wet strength, having a filtering capacity between 700 ml/min and 750 ml/min (acc. to Hertzberg).

7 Sampling and preparation of sample

Take precautions not to unnecessarily contaminate the sample. The sampling procedure is not covered by this Method. Make sure that the aliquot of the sample taken to dilution (8.1) is representative of the sample received.

If the concentration of the sample is not known, determine the concentration (dry matter content) of the sample as described in ISO 4119.

8 Washing the sample

8.1 Dilution

Run the whole procedure in duplicate.

Dilute 30 g (oven-dry basis) of the wet sample to 2000 ml using water (5.1). Using a disintegrator (6.1), disintegrate the sample by having the propeller make 30 000 revolutions.

> *Note 1* – A shorter disintegration time, i.e. 10 000 revolutions, may be used provided it can be shown that the change has no influence on the result. The departure from the standard procedure must be reported.

8.2 Filtration

Immediately after disintegration, withdraw, while stirring continuously the disintegrated pulp suspension (8.1), a volume of (500 ± 50) ml.

Place a filter (6.3) of known weight in a filtering device (6.2). Filter this volume of the pulp suspension and collect the filtrate in a filtering flask. By suction, remove as much water from the pulp as possible.

Wash the pulp mat left on the filter in the funnel three times with 100 ml of water (5.1), and save the washing filtrate.

Remove the pulp mat, with the filter attached, from the funnel and dry overnight in an oven at 105 °C. Place the pulp mat in a desiccator and allow to attain room temperature. From the total weight, subtract the weight of the filter and record the amount of oven-dry pulp, *m*, to the nearest 0,01 g.

Transfer the filtrate, combined with the washings, to a 1 litre measuring cylinder. Record the volume as *V* millilitres.

Check that the filtrate is free from fibres and other visible particles. If the end-determination procedures are not performed on the same day, preserve the filtrate using a preservative or by freezing according to the procedure described in the end determination method, see the chosen method.

> *Warning* – Fibres present in the filtrate will cause results that are too high. Make sure that there are no fibres present in the filtrate after the filtration. If fibres are visible, filter the filtrate once more through a new filter.

8.3 Blank test

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

> *Note 2* – The value of the blank is often below the lower limit of determination.

9 End determination of COD and TOC

9.1 COD determination

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

9.2 TOC determination

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

10 Calculation

10.1 Correct the mass concentration of COD in the filtrate for any disturbance from peroxide residue or chlorate residue (see *Warning 2* in Introduction).

10.2 Calculate the COD or TOC removable by washing, in kilograms per tonne oven dry pulp, using the expression:

$$Y = \frac{V \cdot (X - X_{\mathrm{o}})}{m \cdot 1000} \qquad [1]$$

where

Y is the COD or TOC removable by washing, in kilograms per tonne oven dry pulp;
X is the corrected mass concentration (10.1) of COD or TOC in the filtrate, in milligrams per litre;
X_{o} is the mass concentration of COD or TOC in the blank, in milligrams per litre;
V is the total volume of water used in the filtration and in the washing, in millilitres;
m is the oven-dry mass of the pulp mat, in grams;
1000 is the numerical factor which brings millilitres to litres.

Calculate the mean of the parallel determinations. The results of the parallel determinations should not deviate by more than 10 % from their mean.

Report results from the determination of COD and/or 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 COD and TOC end-determination procedures, the standard method used;
(d) the results, in kilograms per tonne;
(e) any departure from the standard procedure and any other circumstances which may have affected the results.

12 Precision

The repeatability and the reproducibility of the determination depend to a great extent on the sampling.

12.1 Repeatability

12.1.1 Determination of COD

One laboratory analysed COD removable by washing, in ten samples taken from the same gross sample, with the following results:

Sample type	COD, kg /tonne, (photometric procedure)	
	mean	CV, %
Unbl. hardwood sulphate pulp	107	8,0
Unbl. softwood sulphate pulp	78	9,6

12.1.2 Determination of TOC

One laboratory analysed TOC removable by washing, in ten samples taken from the same gross sample, with the following results:

Sample type	TOC, kg/tonne	
	mean	CV, %
Unbl. hardwood sulphate pulp	38,4	6,0
Unbl. softwood sulphate pulp	29,7	9,1

12.2 Reproducibility

12.2.1 Determination of COD

Six laboratories analysed COD removable by washing (using the photometric procedure or the titrimetric procedure) with the following results:

Sample type	COD, kg /tonne,	
	mean	CV, %
Unbl. hardwood sulphate pulp	106	7,8
Unbl. softwood sulphate pulp	81	12,3

The reproducibility results are calculated from the mean values of duplicate determinations, carried out at each laboratory.

12.2.2 Determination of TOC

Four laboratories analysed TOC removable by washing with the following results:

Sample type	TOC, kg/tonne	
	mean	CV, %
Unbl. hardwood sulphate pulp	40,4	5,2
Unbl. softwood sulphate pulp	31,7	4,1

13 Literature

13.1 Laboratoriehandledning för bestämning av COD i blekerifiltrat med Dr Langes kyvett-test, Intern STFI-rapport, Tillämpad kemi, VKB, nr 22, 1997 (In Swedish only)

13.2 SCAN-C 30 Sodium content of wet pulp (withdrawn)

13.3 Ala-Kaila K., Nordén H.V., Leaching of organic material in washing after oxygen delignification, Nord Pulp Paper Res. J., Vol 12 (1997) No 2, *p*94-102

Note – The reference (13.1) is to a "STFI-rapport" written in Swedish. The results are nowadays available to everyone.

Annex A
Situation when an incorrect COD balance may be obtained

If the COD measurements according to SCAN-CM 45 are to be used in calculation of washing efficiency, please note the following:

The analysed COD values will in some situations be wrong. This is most pronounced for a press washer or a dewatering press due to the high pulp consistency in the outlet. In *Figure 1* a typical situation is described.

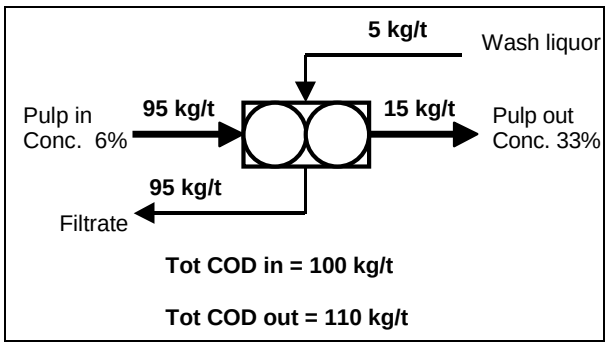

Figure 1. Measured and incorrect COD balance for a press washer.

The balance is incorrect and COD seems to be formed during the press operation, which of course is not true.

The error is in the analysis of COD in pulp, and the explanation is that the analysis sometimes is affected by the concentration of the analysed sample. By the diluting and mixing stage of the analysis, a pulp having a high concentration gives lower COD concentration and ionic strength in the liquor. This lower ionic strength will enhance the COD leaching from the fibre, resulting in a higher COD value and an incorrect COD balance, see Figure 1.

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.
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