SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

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Effluents from pulp and paper mills

Determination of EDTA and DTPA

1 Scope

This SCAN-test Method describes a procedure for the determination of EDTA and DTPA in effluents from pulp and paper mills. The Method can also be used for process waters, e.g. bleaching filtrates.

The limit of detection is 0,05 mg/l using an NPD-detector and 0,5 mg/l using an FID or an MS detector.

2 Reference

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3 Definitions and abbreviations

3.1 For the purpose of this method the following definitions apply:

3.1.1 *EDTA content* – The mass, in hydrogen form, of ethylenediaminotetraacetic acid per volume of water analysed according to this method.

3.1.2 *DTPA content* – The mass, in hydrogen form, of diethylenetriaminopentaacetic acid per volume of water analysed according to this method.

3.2 For the purpose of this method the following abbreviations apply:

GC = gas chromatography
MS = mass spectrometry
FID = flame ionisation detector
NPD = nitrogen/phosphorus detector

4 Principle

The complexing agents, EDTA and DTPA, in a water sample are derivatized with boron trifluoride in methanol and transferred to chloroform by liquid-liquid extraction. The end determination is performed using gas chromatography (GC/FID, GC/NPD or GC/MS).

5 Chemicals and reagents

All chemicals must be of analytical grade.

5.0 *Water* of high purity, de-ionized or distilled.

5.1 *Boron trifluoride in methanol,* between 10 % and 12 % of BF_3.

5.2 *Sodium hydroxide,* 10 mol/l. Dissolve 40 g NaOH in 100 ml of water (5.0).

5.3 *Sodium hydroxide,* 0,1 mol/l. Take 1 ml of the solution 5.2 and dilute to 100 ml with water (5.0).

5.4 *Hydrochloric acid,* HCl, 1 mol/l.

5.5 *Concentrated hydrochloric acid,* HCl.

5.6 *Potassium hydrogen phosphate solution,* 1 mol/l. Dissolve 13,6 g KH_2PO_4 in 100 ml of water (5.0).

5.7 *Buffer solution,* pH 7. Add sodium hydroxide (5.2) to potassium hydrogen phosphate solution (5.6) until pH 7 is reached.

5.8 *Chloroform,* $CHCl_3$.

5.9 *Sodium sulphate,* water-free, Na_2SO_4.

5.10 *Enzyme "catalase"*.

5.11 *Internal standard, CDTA (cyklohexanediamino-tetraacetic acid) stock solution*

If FID or MS is used: 1,0 g/l

If NPD is used: 0,2 g/l.

Weigh to the nearest 0,1 mg approx. 100 mg of CDTA into a volumetric flask and dissolve in a few ml of sodium hydroxide (5.3) and fill up with water (5.0) to 100 ml if FID or MS is to be used, and to 500 ml if NPD is to be used.

5.12 *Internal standard, CDTA*

If FID or MS is used: 10 mg/l

If NPD is used: 2 mg/l

Pipette 1 ml of the solution 5.11 into a 100 ml volumetric flask and fill up to the mark with water (5.0).

5.13 *EDTA, ethylenediaminotetraacetic acid* (MM 292,24)

Note 1 – Also EDTA in salt form *ethylenediamino-tetraacetic acid*, disodium salt × 2 H_2O may be used..

5.14 *DTPA, diethylenetriaminopentaacetic acid*, (MM 393,35)

Note 2 – Also DTPA in salt form (*diethylenetriamino-pentaacetic acid*, calcium trisodiumsalt × H_2O) may be used. The DTPA salt is hygroscopic and should be dried before use.

5.15 *EDTA and DTPA calibration stock solution.* Weigh approx. 125 mg of EDTA (5.13) and 125 mg of DTPA (5.14) with an accuracy of 0,1 mg in a 1000 ml volumetric flask, dissolve in a few millilitres of sodium hydroxide (5.3) and fill up to the mark with water (5.0).

5.16 *EDTA and DTPA calibration solution.* Pipette 2 ml of the solution 5.15 into a 100 ml volumetric flask and fill up to the mark with water (5.0).

Note 3 – If the solutions 5.11 and 5.15 are kept in dark bottles in a refrigerator, the solutions may be stored for at least 3 months. If the solutions 5.12 and 5.16 are kept in dark bottles in a refrigerator, the solutions may be stored for at least 1 month.

Note 4 – If the water contains metal ions, especially iron, the durability of the solution is decreased.

6 Apparatus

6.1 *Indicator paper,* peroxide-sensitive.

6.2 *Balance,* capable of weighing to the nearest ±0,0001 g.

6.3 *Pipettes*, capable of measuring between 10 µl and 5000 µl.

6.4 *Drying oven* or *heating block* capable of maintaining a temperature of 105 °C.

6.5 *Filter paper,* Munktell No 3, or equivalent.

6.6 *Centrifuge,* provided with an angle rotor for 15 ml tubes.

6.7 *Büchner funnel* with a device for vacuum filtration.

6.8 *Centrifuge tubes*, volume 15 ml, with a rounded bottom and provided with a screw cap, heat-resistant up to 105 °C.

6.9 *Gas chromatograph* with FID, NPD or MS as a detector and having a data-sampling software program.

An example of GC-column: DB-5 (5 % of diphenyl/95 % of dimethyl siloxane).

7 Sample preparation

Store the water samples in a refrigerator or a freezer. If the sample contains hydrogen peroxide; remove the peroxide prior to the analysis, preferably already in the sampling procedure, e.g. by adding approx. 10 µl enzyme "catalase" (5.10) per 5 ml of sample. Using an indicator paper (6.1), check that the hydrogen peroxide has been removed.

8 Procedure

8.0 *Blank*. Carry out a blank by analysing 10 ml of water (5.0).

8.1 *Sample*. Take 10 ml of the water sample and centrifuge or filter the sample through a filter paper (6.5) in a Büchner funnel using a device for vacuum filtration.

8.2 Adjust the pH to between 2 and 3, using hydrochloric acid (5.5).

8.3 **FID:** Pipette 5 ml of the sample into a centrifuge tube (6.8) and add 1 ml of CDTA internal standard (5.12).

NPD: Pipette 500 µl of the sample into a centrifuge tube (6.8) and add 500 µl of CDTA internal standard (5.12).

Note 1 – If compounds are present that interfere with the chromatography, the sample should be washed using chloroform (5.8) prior to 8.3, in order to remove these compounds.

8.4 Evaporate the sample to dryness in nitrogen or in a drying oven (6.4) at 105°C.

8.5 Add 1 ml of boron trifluoride in methanol (5.1) to the dried sample, and leave the sample in a closed tube in the drying oven at approx. 105 °C for 1 h.

8.6 Let the sample cool down, add 2 ml of chloroform (5.8) and 3 ml of buffer solution (5.7). Shake the sample vigorously and separate the organic phase (if necessary by centrifuging) from the water phase. Remove the water phase using a pipette.

8.7 Dry the organic phase with sodium sulphate (5.9).

8.8 Inject the sample into the gas chromatograph (6.9). Suggested temperature programme: 200 °C, 10 °C/min to 300 °C, let stand for 2 minutes.

Note 2 – Store the sample in a refrigerator until analysis. The sample should be analysed within 24 h.

Note 3 – If the EDTA or DTPA content is outside the calibration range, adjust the volume of the sample and repeat the procedure from 8.3.

Run the gas chromatograph and record the FID, MS or NPD chromatogram. Record the size of the areas corresponding to the CDTA internal standard and to the EDTA and/or DTPA.

9 Response factor

9.1 Prepare three calibration samples: Take 250 µl, 500 µl, and 1000 µl of the calibration solution 5.16. Add between 2 drops and 3 drops of hydrochloric acid (5.5) and 1 ml of CDTA internal standard (5.12). Analyse according to 8.4-8.8.

Calculate the response factor, *rf,* from the ratio of the CDTA internal standard to the EDTA and DTPA respectively.

10 Calculation

Calculate the exact content of the complexing agents in the hydrogen form from the expression:

$$x = rf \cdot \frac{Ap}{Ai \cdot Ci} \cdot \frac{1000}{V} \qquad [1]$$

where

x is the content of EDTA and/or DTPA, in milligram per litre;
rf is the response factor (9.1);
Ap is the size of the EDTA and/or DTPA area;
Ai is the size of CDTA internal standard area;
Ci is the content of CDTA internal standard, in milligram per litre;
V is the volume of the sample, in millilitres.

Report the content of EDTA and/or the content of DTPA (in hydrogen form) in milligram per litre with one decimal for contents below 100 mg/l and with three significant figures for contents exceeding 100 mg/l.

11 Report

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

(a) date and place of testing;
(b) identification of the sample;
(c) the result according to 10;
(d) the method of analysis (FID, NPD or MS);
(e) any departure from the standard procedure and other circumstances that may have affected the result.

12 Precision

12.1 Repeatability

One laboratory carried out eight parallel determinations. The results are given in the tables below. Filtrate Qa is a diluted Q-stage with addition of DTPA.

Repeatability for EDTA

Sample	EDTA content mean, mg/l	Coefficient of variation, %
Filtrate Qa	8,3	5,2
Q-stage filtrate	37,7	3,2

Repeatability for DTPA

Sample	DTPA content mean, mg/l	Coefficient of variation, %
Mill effluent	1,5	5,4
Filtrate Qa	8,8	4,4

12.2 Reproducibility

The reproducibility, expressed as the coefficient of variation, for the determination of EDTA and DTPA respectively in a mill effluent and in a filtrate from a Q-stage are shown in the tables below. Between five and seven laboratories participated.

Reproducibility for EDTA

Sample	EDTA content mean, mg/l	Coefficient of variation, %
Mill effluent A1	2,9 (7)	13,1
Mill effluent A2	2,9 (6)	9,6
Q-stage filtrate	113 (5)	10,5

The figures within brackets are the number of approved results from the participated labs.

Reproducibility for DTPA

Sample	DTPA content mean, mg/l	Coefficient of variation, %
Mill effluent A	2,7 (5)	29,5
Mill effluent B	5,3 (5)	12,1
Q-stage filtrate	146 (4)	15,9

SCAN-test Methods are issued and recommended by the central laboratories of the pulp, paper and board industries in Finland, Norway and Sweden.
Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604,
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