



## *Effluents from pulp mills*

# Determination of chlorates

### 1 Scope and field of application

This SCAN-test Standard describes a procedure for determining chlorates in effluents from pulp mills producing bleached chemical pulp. The Standard is intended for and is applicable to samples taken from effluents leaving a mill, the purpose being to measure discharges to the recipient. For samples taken within a mill or from a connected biological treatment plant, certain precautions may be necessary to prevent decomposition of chlorate.

*Note 1* – In samples taken in the bleaching plant, chlorine dioxide may be present and reactive so that chlorate can be produced after the sample has been taken. Aeration should remove this chlorine dioxide.

In aeration ponds, anaerobic bacteria may have been induced to reduce chlorate to chloride. Samples from aeration ponds should therefore be aerated to introduce an ample supply of oxygen and then immediately frozen, for example by using a cooling mixture of acetone and solid carbon dioxide.

In some mills, sulphite or sulphur dioxide is used to reduce the chlorate content of the effluent. This should be observed when the sample is analysed. Excess sulphite may interfere in the ion-chromatographic determination of chlorate.

Under unfavourable conditions in the bleaching plant, chlorite may be formed. If a sample containing chlorite is allowed to stand there is a risk that the chlorite will be oxidized to chlorate.

The optimal range of the determination is from 0,5 to 10 mg/l. Samples having a chlorate content exceeding 10 mg/l have to be diluted before analysis.

The limit of detection depends on the matrix and on the type of ion-chromatograph used. For pulp mill effluents, the limit is generally about 0,2 mg/l.

*Note 2* – Nitrate ions may interfere in the determination and any nitrate present will then be determined as chlorate at a mol ratio of approximately 1:1. In effluents from mills using chlorine dioxide in the bleaching plant, the chlorate content normally greatly exceeds the nitrate content and the error can be neglected. If there is reason to believe that the nitrate content is more than negligible, a column that can separate nitrate from chlorate should be used in the ion-chromatograph.

### 2 Definition

*Chlorates (in pulp mill effluents)* – The amount of the chlorate ion,  $\text{ClO}_3^-$ , present in a pulp mill effluent and determined as specified in this Standard.

### 3 Principle

A spot-sample is aerated and either analyzed the same day or preserved by freezing. The chlorate content is determined in filtered samples by means of ion-chromatography.

## 4 Reagents

All reagents shall be of analytical grade. Use distilled or deionized water for dilution of the samples and in the preparation of reagents.

4.1 *Sodium chlorate stock solution*, 1000 mg of chlorate ion per litre. Dissolve 1,273 g of dry sodium chlorate, NaClO<sub>3</sub>, in water and make up to 1000 ml in a volumetric flask.

4.2 *Diluted sodium chlorate solution*, 20 mg/l, for calibration. Transfer 20,0 ml of the sodium chlorate stock solution (4.1) to a 1000 ml volumetric flask and make up to the mark with water. Do not use diluted sodium chlorate solutions that are more than 1 week old.

4.3 *Further solutions*, as specified in the operating instructions for the ion chromatograph.

## 5 Apparatus

5.1 *Sampling bottles*, 250 ml, of chemically resistant glass or polyethylene with plastics-lined screw caps. If the samples are to be preserved by freezing, use polyethylene bottles that withstand freezing.

5.2 *Ion-chromatograph* having a pump, an injector loop of known volume, a column system and a conductivity detector. The column should be capable of separating chlorate ions from other anions present.

*Note* – On some columns, nitrate ions will not be separated from chlorate ions. Such columns should not be used unless it has been ensured that the interference from nitrate will be negligible. (In most mill effluents only very small amounts of nitrate are present.)

If sulphite ions are present (see Clause 1), check that the column separates sulphite ions from chlorate ions or destroy excess sulphite by adding a few drops of hydrogen peroxide.

5.3 *Syringe* having a pre-filter of 0,22 µm pore width.

## 6 Sampling and sample preservation

Samples for chlorate determination shall be collected with the usual care to ensure that they are representative of the effluent stream under study. Use either glass bottles or new polyethylene bottles (5.1). Fill the bottles half-full. Close the bottles and aerate by shaking vigorously for about 20 s. Repeat the aeration at least once.

*Note 1* – It is important to increase the oxygen content in the sample to avoid microbiological degradation of chlorate present.

Preserve samples taken downstream of a biological treatment plant by freezing them immediately, for example in a cooling mixture of acetone and solid carbon dioxide.

Preserve also samples taken in other positions if they cannot be analysed on the day of sampling.

Keep frozen samples at a temperature below -18 °C until required for analysis.

Do not use composite-samples for chlorate determination.

Ensure that the samples taken are free from active chlorine.

*Note 2* – Normally effluents from bleaching plants are free from active chlorine. To test for the presence of active chlorine, use the following procedure: Transfer a few millilitres of an acidified sample to a test tube. Dissolve a few crystals of potassium iodide (KI) in the sample and add a few drops of a 1 % starch solution. A blue colour indicates the presence of active chlorine. Other oxidants may give the same reaction. Active chlorine can be removed by stripping with nitrogen.

*Note 3* – Samples containing microorganisms may lose their chlorate ions due to microbiological activity. It is thus important that such activity is prevented by aeration and preservation immediately after sampling. Composite-samples taken by automatic sampling devices may contain microorganisms, even in mills without biological treatment plants, and their chlorate content may decrease during the sampling period. Therefore only use spot-samples for the determination of chlorate.

## 7 Preparation of sample portions

Thaw frozen samples by keeping them at room temperature, preferably in a water bath of room temperature, for the time required. Do not heat the sample further. The analysis of the thawed sample must be carried out on the same day as the thawing.

Run the determination in duplicate. It is essential that the sample portion is free from suspended matter. Therefore use the syringe (5.3).

The sample solution taken to analysis should have a chlorate content within the optimal range of the ion-chromatograph. Normally it is necessary to dilute the sample to reach this range. When diluting, do not use less than 5 ml of the original sample. Record the dilution factor (final volume divided by original volume).

If the dilution factor is greater than 10, dilute in two or more steps.

*Note 1* – Overloading the column reduces its lifetime. With unknown samples, make a trial run with a test portion of great dilution factor (for example 100). Repeat the trial with samples of decreasing dilution factors until the optimum working level has been reached. Never use an undiluted test portion of an unknown sample.

*Note 2* – In some systems it is preferable to dilute the sample with the same solution as that used as the mobile phase. If this procedure is used, the calibration solutions should be prepared in the same manner.

## 8 Procedure

Since the procedure depends on the design of the chromatograph, no detailed instructions can be given here. Operate the apparatus as instructed by the manufacturer.

For calibration, prepare from the diluted sodium chlorate solution (4.2) a series of 5 calibration solutions, covering about one decade of concentrations, for example from 1 to 10 mg/l, see Clause 7, Note 2. Run the calibration solutions as instructed in the ion-chromatograph manual and prepare a calibration graph. The 5 points on the graph should fall on a straight line. If there are indications after repeated runs, that the points are on the unlinear part of the calibration curve, the calibration shall be repeated with another set of calibration solutions, covering a lower or higher concentration range, as relevant.

Repeat the calibration regularly and whenever new diluted sodium chlorate solutions (4.2) are taken into use.

Check the calibration several times daily by running one of the calibration solutions.

*Note* – Since the calibration curve is linear, only one calibration solution is required for the daily control.

## 9 Calculation and report

Read the chlorate concentration from the calibration graph. Multiply the reading by the dilution factor.

Report the mean in milligrams per litre to the first decimal place. If the mean is below 1 mg/l, report the result to the second decimal place. If the mean is higher than 10 mg/l report the result without decimals.

The report shall include a reference to this Standard and the following particulars:

- date and place of testing;
- precise identification of the sample;
- the result;
- if relevant, a note on the presence of interfering substances, as judged from the shape of the chlorate peak in the chromatogram;
- any departure from the standard procedure or any other circumstances that may have affected the result.

## 10 Precision

10.1 *Repeatability.* The repeatability when determining the chlorate content of a chlorate standard solution, expressed as the coefficient of variation, is generally less than 2 %.

10.2 *Reproducibility.* Nine laboratories determined the chlorate content in different samples taken from effluents from a pulp mill. The reproducibility, measured as the coefficient of variation, was as follows:

Sample	Mean chlorate content, mg/l	Coeff. of variation, %
Bleach plant effluent	147	4,0
Total effluent mixed with chlorate	1,1	10,5
Chlorate standard	48	7,0
Mixed effluents	38	7,0
Total effluent mixed with chlorate	10	7,0

**SCAN-test Standards are issued and recommended by the central laboratories of the pulp, paper and board industries in Denmark, Finland, Norway and Sweden.**

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