SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

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Process waters

Cationic demand

Polyelectrolyte titration with a streaming current detector

0 Introduction

Process waters often contain dissolved and colloidal material that is anionically charged and that may react with cationic additives used in the papermaking process. The amount of such anionic material may be determined by a titration using a cationic polymer as titrant. The result is often called the "Cationic Demand" as it is related to the "demand" for cationic polymers. More correctly expressed, the value is related to the consumption of the cationic titrant, which is used in the titration. As the anionically charged material may react in different ways with different cationic polymers, the Cationic Demand value is to be considered as an empirical value that is defined by the method used.

1 Scope

This SCAN-test Method describes a procedure for the determination of cationic demand in all types of process waters in pulp and paper mills.

The method is not applicable for the determination of the cationic demand in process waters containing fibres or fines. Prior to the determination, fibres and fines must be removed.

> *Note 1* – In some cases, it may be desired to determine the cationic demand in fines-containing samples. In such cases, the titration method described in this SCAN-test method can be used. However, a suitable procedure for preparing a sample with a relevant content of fines is not covered by this method.

The method is not applicable to samples having a high conductivity. The conductivity of the sample should not exceed 500 mS/m (5000 µS/cm). Subclauses 7.3 and 8.4 give more information about the effects of high conductivity.

It is not possible to determine anionic polymers with a very low molecular mass, or oligomers, using this method.

> *Note 2* – The user is recommended to check with the manufacturer the range of conductivities that the instrument can handle.

2 References

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3 Definitions

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

3.1 *Cationic demand* – The amount of cationic polymer consumed at the equivalence point of a polyelectrolyte titration.

3.2 *Equivalence point* – The point where the measured potential passes zero during the polyelectrolyte titration.

3.3 *Fines* – Particles passing through a 200 mesh or a 76 µm wire.

4 Principle

The sample, free from fibres and fines, is titrated with a cationic polymer of known charge concentration using a streaming current detector to detect the equivalence point. Under the conditions used, it is assumed that the cationic polymer and the anionic polymer(s) in the sample are forming 1:1 complexes.

5 Reagents and chemicals

All chemicals must be of analytical grade.

5.1 *Deionised water* or *distilled water*.

5.2 *PolyDADMAC solution*, DiallylDimethylAmmoniumChloride, e.g. 1 meq[1]/l, as the titrant.

Prepare a solution with a charge concentration of approximately 10 meq/l using a polyDADMAC with a charge density of about 6,2 meq/g and with a well-defined molecular mass distribution. The average molecular mass, $M_{w,}$ should be between 50 000 and 500 000. Dilute the polyDADMAC solution with deionised water (5.1) to a suitable charge concentration, e.g. 1 meq/l.

Note 1 – Certified polyDADMAC solutions with a concentration of 1 meq/l are available on the market.

Note 2 – If the molecular mass distribution, M_w, of the polyDADMAC is outside the recommended interval, it may affect the determined cationic demand value. This is especially true for low molecular mass polyDADMACs.

The polyDADMAC solution is stable at room temperature (approx. 23 °C) for at least 6 months.

5.3 *PES-Na solution,* PolyEtheneSodiumsulphonate, for instrument check and calibration of the titrant.

Use a solution of PES-Na of approx. 1 meq/l known to an accuracy of 0,001 meq/l.

Note 3 – PES-Na solutions with a concentration of 1 meq/l are available on the market.

Store the PES-Na solution in the dark at 4 °C. It is stable for at least 6 months.

5.4 *Sodium bromide*, NaBr, for the cleaning solution.

5.5 *Acetone,* for the cleaning solution.

5.6 *Cleaning solution*, for cleaning of the sample cell. Dissolve 50 parts (by weight) of sodium bromide (5.4) in 125 parts (by weight) of deionised water (5.1). Carefully, add 50 parts (by weight) of acetone (5.5).

Note 4 – Sometimes, the sample cell is preferably cleaned using a common mineral acid or base.

6 Apparatus

6.1 *Process-sampling and filtering device,* consisting of a small cylinder with a wire of a suitable mesh size attached or welded to its bottom. The mesh size of the wire may be 76 µm or larger (e.g. 300 µm)

or, if this is not available,

6.2 *Dynamic Drainage Jar,* DDJ (ref. 12.2), equipped with a 76 µm wire, for removing the fibres from the sample if they have not been removed during sampling.

6.3 *Centrifuge*, with a capacity to centrifuge at 500 *g*, to remove the fines from the sample

or, if this is not available,

6.4 *Filtering device,* consisting of:

6.4.1 *Büchner funnel*.

6.4.2 *A filter paper*, to remove the fines from the sample.

Before use, check that the filtration gives the same results as the centrifugation.

6.5 *Precision burette,* for adding the titrant to the test portion.

6.6 *Streaming current detector.* The most common equipment consists of a Teflon sample cell in which a Teflon piston oscillates. This movement generates a potential, which is measured.

6.7 *PC or other equipment,* for recording the titration curve (optional).

6.8 *pH meter.*

6.9 *Conductivity meter.*

7 Sampling and pre-treatment

7.1 Sampling

The sampling procedure is not covered by this method. Make sure that the test portions taken are representative of the sample received.

[1] meq = milliequivalents

7.2 Sample pre-treatment

As soon as possible after sampling, remove the fibres from the sample since they are considered to affect the cationic demand of the sample. The fibres can be removed directly at the time of sampling, preferably by using the process-sampling and filtering device (6.1). During sampling, the device is submerged into the stock or process water, thereby letting a water sample flow into the cylinder free from fibres.

Take a test portion of between 100 ml and 200 ml of this water sample for further pre-treatment.

The fibres may also be removed by using a DDJ (6.2) or, in the case of high fibre consistency, by filtration in a Büchner funnel (6.4.1) without any filter.

As soon as possible, remove the fines from the water phase by centrifuging (6.3) the test portion at 500 *g* for 15 min or, if no centrifuge is available, by filtration in a Büchner funnel (6.4.1) with filter (6.4.2).

> *Note* – In some cases, it may be desired to remove the fibres and the fines at the same time in a single filtration. As there is a risk that colloidal material is also removed by this filtration, it is recommended to check that this procedure gives the same result as the method where the fibres and the fines are removed consecutively.

7.3 Check of pH and conductivity

Measure the pH and the conductivity of the test portion to be analysed.

As pH and conductivity may affect the results, it is important to measure and record these two parameters. A high pH may result in a higher cationic demand and a high conductivity will decrease the initial potential reading and change the appearance of the curve.

7.4 Sample storage

Carry out the analysis as soon as possible after sampling. In the test report, include the sampling date and time, the titration date and time and the storage method.

8 Procedure

8.1 Cleaning procedure

Clean the sample cell after each titration with deionised water (5.1) and a soft test tube brush and at least once a day with a cleaning solution (5.6). Be careful not to scratch the surface of the cell. Let the sample cell stand with a cleaning solution for approx. 1 min. Wash the sample cell with deionised water (5.1) and gently clean with a soft test tube brush. When not in use, store the sample cell in distilled water or in air. In the latter case, the sample cell should be immersed in deionised water for at least 1 h before the measurement.

8.2 Instrument check

Check the function of the instrument (6.6) each month or according to the supplier recommendation.

As described in 8.4, make a titration using e.g. 10 ml of PES-Na solution (5.3) as sample. If a titrant with a concentration of 1 meq/l is used, the consumption of polyDADMAC solution shall be between 9,5 ml and 10,5 ml.

8.3 Calibration of titrant

Calibrate the titrant (5.2) with PES-Na solution (5.3) at least once a month and when a new titrant is used.

As described in 8.4, make a titration, using e.g. 10 ml of PES-Na solution (5.3) as sample. Calculate the charge concentration of the polyDADMAC solution according to 9.1.

8.4 Determination of cationic demand

Carry out the procedure in duplicate. Pipette or weigh *m* g of the (undiluted) test portion into the sample cell. Insert the sample cell in the instrument (6.6). Place the burette tip above the test portion surface, wait for about 1 min, and start the titration. The time between the titrant additions should be at least 30 s. It is recommended that the number of titrant additions is approx. 10.

The total volume of added titrant should not exceed 30 % of the original volume of the test portion as dilution of the test portion may result in a lower cationic demand value. If the volume of the added titrant exceeds the recommended 30 % dilution, adjust the charge concentration of the polyDADMAC solution (5.2) used as titrant.

Record the consumed volume of polyDADMAC solution, *V*, at the equivalence point (i.e. at zero potential). If a titration curve is recorded, save it.

Check the result from the first titration of the day. If the results from the parallel test portion diverge too much, perform a new analysis.

> *Note 1* – To save time, a pre-dose of the titrant may be added before the actual titration is started. In most cases, a waiting time after the pre-dose of at least 2 min is sufficient.

> *Note 2* – If the sample has a high conductivity, the titration curve may be distorted, and this will in some cases lead to unreliable results.

9 Calculation

9.1 Charge concentration of the titrant

Calculate the charge concentration of the polyDADMAC solution from the expression:

$$c = \frac{a \cdot b}{d} \qquad [1]$$

where
c is the charge concentration of polyDADMAC solution, in milliequivalents per litre;
a is the charge concentration of the PES-Na solution, in milliequivalents per litre;
b is the volume of the PES-Na solution, in millilitres;
d is the consumed volume of polyDADMAC solution, in millilitres.

9.2 Cationic demand of the sample

Calculate the cationic demand of the sample from the expression:

$$X = \frac{c \cdot V \cdot \rho}{m} \cdot 1000 \qquad [2]$$

where
X is the cationic demand, in microequivalents per litre;
c is the charge concentration of the polyDADMAC solution, in milliequivalents per litre;
V is the consumed volume of the polyDADMAC solution, in millilitres;
m is the weight of the test portion, in gram;
ρ is the density of the process-water sample, in gram per millilitres. The density is in most cases approximately 1.

Calculate the mean cationic demand. Report the result in microequivalents per litre.

10 Report

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

(a) date and time of sampling;
(b) date and time of titration;
(c) the storage method;
(d) identification mark of the sample;
(e) the state of the sample analysed (without fines or, in special cases, with fines);
(f) details about the method used when removing the fines;
(g) pH and conductivity of the sample;
(h) the titration curve (optional);
(i) the cationic demand;
(j) any departure from the standard procedure and any other circumstances that may have affected the results.

11 Precision

Two laboratory-prepared process-water samples and five different white water samples (WW) were analysed in an interlaboratory study comprising seven laboratories and five laboratories respectively.

11.1 Repeatability

Each laboratory tested each sample five times. The average coefficient of variation (CV within lab) between replicates was 1,7 %. See the table for details.

11.2 Reproducibility

The results from the laboratories had an average coefficient of variation (CV between labs) of 5,8 %. The results are shown in the table.

Sample	No of labs	Mean cationic demand, µeq/l	CV within lab, %	CV between labs, %
CMC solution	7	286	1,0	1,5
Preparation from CTMP	7	187	1,9	4,5
WW from a LWC paper mill	4	85	3,1	11,9
WW from a newsprint mill	4	276	1,2	4,8
WW from a LWC paper mill	5	297	1,7	4,8
WW from a newsprint mill	5	260	1,2	3,2
WW from a board mill (unbl.)	5	112	2,1	10,0
Average value			1,7 %	5,8 %

12 Literature

12.1 T. Ojala (1993). Charge measurements of different furnishes using polyelectrolyte titration with a streaming current detector. Tappi Papermakers Conference, Atlanta, GA (USA).

12.2 TAPPI (1980). TAPPI Test Method T 261 pm-80. Fines Fraction of Paper Stock by Wet Screening, Tappi.

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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