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ISO RECOMMENDATION

R 692

PULPS

DETERMINATION OF ALKALI SOLUBILITY

1st EDITION
March 1968

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BRIEF HISTORY

The ISO Recommendation R 692, *Pulps – Determination of alkali solubility*, was drawn up by Technical Committee ISO/TC 6, *Paper, board and pulps*, the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question by the Technical Committee began in 1962 and led, in 1964, to the adoption of a Draft ISO Recommendation.

In December 1965, this Draft ISO Recommendation (No. 886) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina
Australia
Belgium
Brazil
Canada
Chile
Colombia
Czechoslovakia
Denmark
Finland
France
Germany
India
Iran
Ireland
Israel
Italy
Japan
New Zealand
Norway
Poland
Portugal
Romania
South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
U.A.R.
United Kingdom
U.S.A.
Yugoslavia

One Member Body opposed the approval of the Draft :

Netherlands

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council which decided, in March 1968, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 692 March 1968

PULPS

DETERMINATION OF ALKALI SOLUBILITY

FOREWORD

The object of both this ISO Recommendation and of ISO Recommendation R 699, *Pulps – Determination of alkali resistance,* is to permit the study of the behaviour of pulps in the presence of alkali solutions, but their fields of application are different : while this ISO Recommendation describes the volumetric determination of the alkali soluble constituents of the pulp and is applied preferably to the control of bleached pulps, ISO Recommendation R 699 describes the gravimetric determination of the alkali insoluble constituents and applies to all categories of pulp.

1. SCOPE

This ISO Recommendation describes a method for determining the solubility of pulp in cold sodium hydroxide solutions of various and fixed concentrations. The concentrations of sodium hydroxide solutions most frequently used are 18 and 10 % (m/m).

2. FIELD OF APPLICATION

This method is mainly intended for investigation of bleached pulps, but may, however, also be used with unbleached pulps, for example in the different stages of manufacture of bleached pulp.

3. PRINCIPLE OF THE METHOD

Pulp is treated with sodium hydroxide solution and the dissolved organic matter is oxidized with potassium dichromate. Excess potassium dichromate is determined volumetrically and the cellulose amount equivalent to the potassium dichromate consumed is calculated.

4. DEFINITION OF TERMS

4.1 S – *value.* Alkali solubility : the soluble fraction expressed as a percentage of the oven-dry pulp mass.

4.2 S_{18}, S_{10} or S_c. S-values in which the indices 18, 10 or c refer to the chosen concentration expressed in grammes of sodium hydroxide per 100 g of solution.

5. REAGENTS

All reagents should be of analytical grade.

5.1 *Sodium hydroxide solution*, of known concentration, containing less than 1 g per litre of sodium carbonate (see Note below), for example :

- sodium hydroxide solution, 5.39 ± 0.03 M, containing 18.0 ± 0.1 g of sodium hydroxide (NaOH) per 100 g of solution ($\rho_{20} = 1.1972$ g/cm^3), equivalent to 215.5 ± 1.0 g of sodium hydroxide (NaOH) per litre.
- sodium hydroxide solution, 2.77 ± 0.03 M, containing 10.0 ± 0.1 g of sodium hydroxide (NaOH) per 100 g of solution ($\rho_{20} = 1.1089$ g/cm^3) equivalent to 110.9 ± 1.0 g of sodium hydroxide (NaOH) per litre.

NOTE. – The sodium hydroxide solution is conveniently prepared as follows :

Dissolve a quantity of solid sodium hydroxide in an equal mass of distilled water and allow the suspended sodium carbonate to settle. Decant the supernatant liquid and dilute with carbon dioxide-free distilled water to the appropriate concentration. Check by titration with standard acid solution.

5.2 *Sulphuric acid*, concentrated, not less than 94 % sulphuric acid (H_2SO_4), ($\rho_{20} = 1.84$ g/cm^3).

NOTE. – If the concentrated sulphuric acid is of lower concentration than 94 %, the temperature will not reach the 125 to 130 °C required during the oxidation.

5.3 *Potassium dichromate solution*, about 0.067 M (= 0.4 N), in 2.7 M sulphuric acid. 20 g of potassium dichromate ($K_2Cr_2O_7$) and 150 ml of sulphuric acid (H_2SO_4) ($\rho_{20} = 1.84$ g/cm^3) per litre of solution.

5.4 *Ammonium iron (II) sulphate solution*, approximately 0.1 N. (Normality known with an accuracy of ± 0.000 2) : 40 to 41 g of ammonium iron (II) sulphate ($FeSO_4\,(NH_4)_2SO_4 \cdot 6H_2O$) and 10 ml of sulphuric acid (H_2SO_4) ($\rho_{20} = 1.84$ g/cm^3) per litre. This solution is not stable and its normality should be checked every day.

NOTE. – In order to restore the original normality of the ammonium iron (II) sulphate solution, a reducing agent can be placed between the supply bottle and the burette.

Preparation of the reducing agent : metallic cadmium (which passes a sieve of 8 to 12 mesh per centimetre) is freed from fine particles by washing with water. The metal is treated for about 5 minutes with a 2 % solution of mercuric nitrate ($Hg\,(NO_3)_2 \cdot H_2O$) or mercuric chloride ($HgCl_2$) containing 5 ml of concentrated nitric acid per litre, and then the amalgamated metal is washed. The ammonium iron (II) sulphate solution may be standardized against potassium dichromate as a primary standard.

The normality of the ammonium iron (II) sulphate solution stays constant when, to a 10 litre bottle, are added 5 g of aluminium shavings of more than 99.99 %.

5.5 *Phosphoric acid*, 85 % ($\rho_{20} = 1.70$ g/cm^3).

5.6 *Ferroin indicator solution*, 15 g per litre of 1 : 10 – phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) or 16 g per litre of 1 : 10 – phenanthroline hydrochloride ($C_{12}H_8N_2 \cdot HCl \cdot H_2O$) and 7 g of iron sulphate ($FeSO_4 \cdot 7H_2O$) per litre of solution, or

5.7 *Sodium diphenylaminosulphonate indicator solution*, 0.1 g sodium diphenylaminosulphonate ($C_{12}H_{10}NSO_3Na$) per 100 ml of water.

6. APPARATUS

6.1 *Stirring equipment,* with a propeller-type agitator made of stainless steel or other corrosion-resisting material. The angle of the blades should be adjusted so that air is not introduced into the pulp suspension during stirring.

NOTE. – Suitable equipment is shown in the Figure below. A satisfactory motor is one of 1/50 horse-power, running between about 1700 and 1450 revolutions per minute.

6.2 *Constant temperature bath,* capable of maintaining a temperature of 20 ± 0.2 °C.

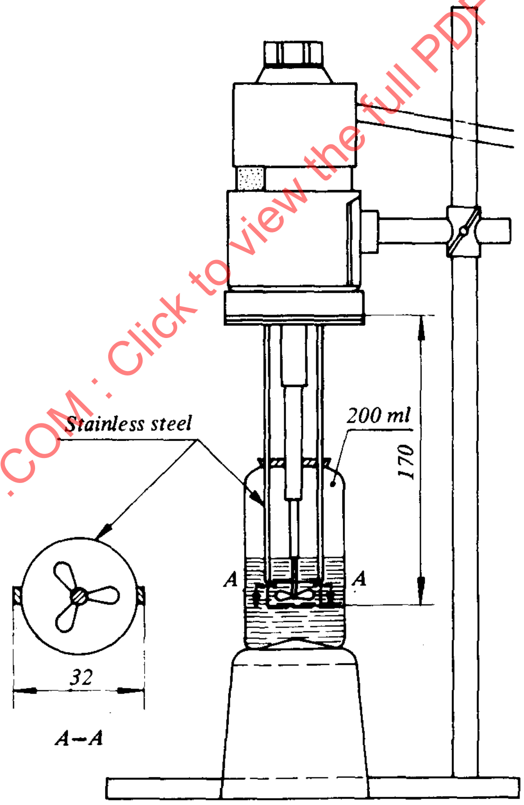
6.3 *Filtering crucibles or funnels,* 50 ml, made of alkali-resistant material, with a sintered glass disc having diameter of pores between 15×10^{-4} cm and 40×10^{-4} cm (G 3).

6.4 *Suction flasks,* for the crucibles or funnels.

6.5 *Balance,* accurate to 1 mg.

6.6 *Reaction vessel,* of 200 ml capacity and tall in shape.

Dimensions in millimetres



7. PREPARATION OF SAMPLE

If the pulp is in sheet form tear into pieces approximately 5 mm × 5 mm. If in slush form, remove water by suction, press between blotters and dry at a maximum temperature of 60 °C. Before weighing the test pieces, condition them for not less than 20 minutes in the atmosphere near the balance.

8. PROCEDURE

Weigh, to the nearest 0.005 g, the equivalent amount of approximately 1.5 g of oven-dry pulp. Then immediately weigh out two test portions for dry matter content determination according to ISO Recommendation R 638, *Pulps – Determination of dry matter content.*

With a pipette, add 100.0 ± 0.2 ml of the chosen sodium hydroxide solution to the tall 200 ml reaction vessel. Adjust the temperature to 20 ± 0.2 °C (see Note 1 opposite) by placing it in the constant temperature bath.

Put the quantity of pulp into the sodium hydroxide solution and allow it to swell for 2 minutes. Stir in the reaction vessel for 3 minutes or until the pulp is completely disintegrated (see Note 2 opposite). Lift the stirrer from the reaction vessel. Some fibres and sodium hydroxide solution may remain on the stirrer when it is removed, but at the low concentration used, this small loss may be neglected. Maintain the reaction mixture at 20 ± 0.2 °C for a period of 60 minutes from the time the pulp was brought into contact with the sodium hydroxide solution.

At the end of 60 minutes, stir the slurry with a glass rod and filter with slight suction through the sintered glass disc in the crucible or funnel* avoiding passage of air through the residue. Reject the first 10 to 20 ml and, in a clean bottle or flask collect the next 40 to 50 ml of the filtrate for testing.

With a pipette, transfer 10.0 ml (see Note 3 opposite) of the filtrate to a 250 ml conical flask. Add with a pipette 10.0 ml of potassium dichromate solution and then carefully add, with swirling, 30 ml of concentrated sulphuric acid. Check that the temperature is between 125 and 130 °C.

Allow the hot solution to remain above 120 °C for 10 minutes to complete oxidation. Cool the flask to room temperature.

According to the case, proceed as follows :

(*a*) To the cold solution, add 50 ml of distilled water. Cool again, add two drops of ferroin indicator solution and titrate with the freshly standardized (see Note to clause 5.4) ammonium iron (II) sulphate solution to a violet colour.

(*b*) Dilute the cold solution with water to a volume of about 100 ml and add 5 ml of the phosphoric acid. Cool again, and titrate rapidly with the freshly standardized (see Note to clause 5.4) ammonium iron (II) sulphate solution until about 90 % of the required amount has been added. Then add by pipette 1 ml sodium diphenylaminosulphonate indicator solution, and titrate further without delay to colour change from dark brown through violet to a bright green (see Note 4 opposite).

Make a blank test, substituting 10 ml of the chosen sodium hydroxide solution for the filtrate and using approximately the same temperature and time to complete the titration (see Note 5 opposite).

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* The filters used should be washed with a sulphochromic mixture, i.e. a potassium dichromate solution in sulphuric acid.

NOTES

1. The solubility in the 18 % sodium hydroxide solution is not affected by variations of a few degrees in temperature. At this concentration, the temperature may be kept at 20 ± 2 °C.

   The solubility in a weaker alkali solution (for example, 10 %) is much more dependent on temperature. At this lower concentration, the temperature of the mixture should be kept at 20 ± 0.2 °C.

2. An increase in stirring time does not significantly affect the alkali solubility, but too low a value will be obtained if disintegration is not complete. Keep stirring, therefore, until the sample is completely disintegrated.

3. When normal dissolving pulps are tested, 10 ml of the filtrate is a suitable aliquot. If the alkali solubility is greater than 16 %, reduce the aliquot to 5 ml and the amount of sulphuric acid to 25 ml. If the alkali solubility is less than 5 %, use 20 ml of filtrate and 45 ml of the sulphuric acid.

   In the blank test use the corresponding volumes of sodium hydroxide solution and sulphuric acid.

4. In excess acid potassium dichromate solution, the indicator is partly oxidized, which not only results in potassium dichromate consumption, but also in other than original colour characteristics. As the oxidation depends on such factors as relative amounts and concentrations of potassium dichromate and indicator, the excess potassium dichromate should be reduced as quickly as possible. This is done most effectively by adding the indicator no sooner than after "neutralization" of about 90 % of the excess potassium dichromate. When the titration is completed without delay, the indicator error has been found negligible.

5. Alternatively an iodometric titration procedure can be used, but its use should be stated with the test results.

   Transfer the cold solution after oxidation to a 1000 ml conical flask, using 500 ml of distilled water. Add 2 g of potassium iodide KI, maintaining the temperature below 10 °C, swirl to dissolve and mix, then allow to stand for 5 minutes. Titrate with standardized 0.1 N sodium thiosulphate solution, $Na_2S_2O_3$, adding powdered starch indicator of analytical grade when the yellow colour of the iodine has nearly disappeared. The end point is indicated by a change from deep blue to light green. Make a blank test, substituting a 10 ml portion of the sodium hydroxide solution for the filtrate. Calculate as described in clause 9.1, substituting for a and b the corresponding volumes of sodium thiosulphate solution and for n the normality of the solution.