INTERNATIONAL STANDARD ISO 692

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION •МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ •ORGANISATION INTERNATIONALE DE NORMALISATION

Pulps — Determination of alkali solubility

Pâtes — Détermination de la solubilité dans les solutions d'hydroxyde de sodium

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 6 has reviewed ISO Recommendation R 692 and found it suitable for transformation. International Standard ISO 692 therefore replaces ISO Recommendation R 692-1968.

ISO Recommendation R 692 was approved by the Member Bodies of the following countries :

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The Member Body of the following country has subsequently approved this Recommendation :

Netherlands

No Member Body disapproved the transformation of ISO/R 692 into an International Standard.

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INTERNATIONAL STANDARD

ISO 692-1974 (E)

Pulps — Determination of alkali solubility

0 INTRODUCTION

The object of both this International Standard and of ISO 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 International Standard describes the volumetric determination of the alkali soluble constituents of the pulp and is applied preferably to the control of bleached pulps, ISO 699 describes the gravimetric determination of the alkali insoluble constituents and applies to all categories of pulp.

1 SCOPE

This International Standard specifies 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 the 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 REFERENCE

ISO/R 638, *Pulps — Determination of dry matter content.*

4 PRINCIPLE

Treatment of the pulp with sodium hydroxide solution and oxidation of the dissolved organic matter with potassium dichromate. Volumetric determination of the excess potassium dichromate and calculation of the cellulose amount equivalent to the potassium dichromate consumed.

5 DEFINITIONS OF TERMS

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

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

6 REAGENTS

All reagents shall be of analytical grade.

6.1 Sodium hydroxide solution, of known concentration, containing less than 1 g/l of sodium carbonate (see note below), for example :

- 5,39 ± 0,03 N, containing 18,0 ± 0,1 g of NaOH per 100 g of solution (ρ_{20} 1,197 2 g/ml), equivalent to 215,5 ± 1,0 g of NaOH per litre.
- 2,77 ± 0,03 N, containing 10,0 ± 0,1 g of NaOH per 100 g of solution (ρ_{20} 1,108 9 g/ml), equivalent to 110,9 ± 1,0 g of 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.

6.2 Sulphuric acid, concentrated, not less than 94 % (*V/V*) sulphuric acid (ρ_{20} 1,84 g/ml).

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.

6.3 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 (ρ_{20} 1,84 g/ml) per litre of solution.

6.4 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 (ρ_{20} 1,84 g/ml) per litre. This solution is not stable and its normality shall 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 min with a 2 % solution of mercury(II) nitrate [$Hg(NO_3)_2 \cdot H_2O$] or mercury(II) 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 l bottle, are added 5 g of aluminium shavings of more than 99,99 % purity.

6.5 Phosphoric acid, 85 % (*V/V*) (ρ_{20} 1,70 g/ml).

6.6 Ferroin indicator solution. 15 g per litre of 1:10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$) or 16 g per litre of 1:10-phenanthroline hydrochloride ($C_{12}H_8N_2.HCl . H_2O$) and 7 g of iron(II) sulphate ($FeSO_4.7H_2O$) per litre of solution, or

6.7 Sodium diphenylaminosulphonate indicator solution. 0,1 g sodium diphenylaminosulphonate ($C_{12}H_{10}NSO_3Na$) per 100 ml of water.

7 APPARATUS

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

NOTE — Suitable equipment is shown in the figure. A satisfactory motor is one of 1/50 horse-power, running between about 1 700 and 1 450 rev/min.

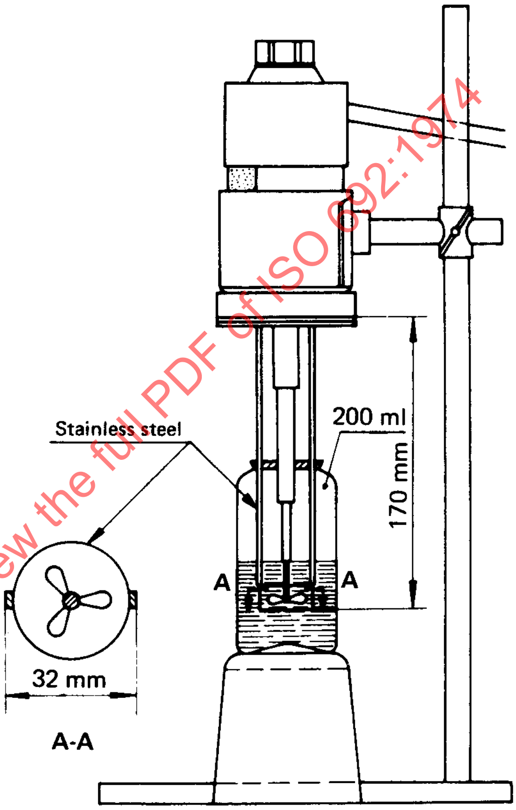
7.2 Constant temperature bath, capable of maintaining a temperature of 20 ± 0,2 °C.

7.3 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 (G3).

7.4 Suction flasks, for the crucibles or funnels.

7.5 Balance, accurate to 1 mg.

7.6 Reaction vessel, capacity 200 ml and tall in shape.



8 PREPARATION OF THE TEST SAMPLE

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

9 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/R 638.

With a pipette, add 100,0 ± 0,2 ml of the chosen sodium hydroxide solution (6.1) to the reaction vessel (7.6). Adjust the temperature to 20 ± 0,2 °C (see note 1) by placing it in the constant temperature bath (7.2).

Put the quantity of pulp into the sodium hydroxide solution and allow it to swell for 2 min. Stir in the reaction vessel for 3 min or until the pulp is completely disintegrated (see note 2). 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 min from the time the pulp was brought into contact with the sodium hydroxide solution.

At the end of 60 min, stir the slurry with a glass rod and filter with slight suction through the sintered glass disc in the crucible or funnel[1] 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) of the filtrate to a 250 ml conical flask. Add with a pipette 10,0 ml of potassium dichromate solution (6.3) and then carefully add, with swirling, 30 ml of concentrated sulphuric acid (6.2). Check that the temperature is between 125 and 130 °C.

Allow the hot solution to remain above 120 °C for 10 min 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 2 drops of ferroin indicator solution (6.6) and titrate with the freshly standardized (see note to 6.4) 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 (6.5). Cool again, and titrate rapidly with the freshly standardized ammonium iron(II) sulphate solution (6.4) until about 90 % of the required amount has been added. Then add by pipette 1 ml of sodium diphenylaminosulphonate indicator solution (6.7), and titrate further without delay to colour change from dark brown through violet to a bright green (see note 4).

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).

Carry out two determinations on each sample.

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 shall 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 must 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 shall be stated with the test results.

Transfer the cold solution after oxidation to a 1 000 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 min. 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 10.1, substituting for V_1 and V_2 the corresponding volumes of sodium thiosulphate solution and for N the normality of the solution.

10 EXPRESSION OF RESULTS

10.1 Method of calculation and formulae

Calculate the alkali solubility, S_c in percent, as follows :

$$\frac{6{,}85\,(V_2 - V_1)\,N \times 100 \times 100}{1\,000 \times m\,V} = \frac{68{,}5\,(V_2 - V_1)\,N}{m\,V}$$

where

V is the volume, in millilitres, of filtrate used in the oxidation;

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[1] The filters used shall be washed with a sulphochromic mixture, i.e. a potassium dichromate solution in sulphuric acid.

V_1 is the volume, in millilitres, of ammonium iron(II) sulphate solution consumed in the titration of the sample;

V_2 is the volume, in millilitres, of ammonium iron(II) sulphate solution consumed in the blank test;

N is the normality of the ammonium iron(II) sulphate solution;

m is the mass, in grams, of the test piece, calculated on the basis of oven-dry pulp;

6,85 is the empirical factor, in milligrams, indicating the amount of cellulose equivalent to one milliequivalent of potassium dichromate (see note below).

NOTE – Theoretically, 1 milliequivalent of potassium dichromate corresponds to 6,75 mg of cellulose or other hexosans, and 6,60 mg of pentosans. In general, the soluble components of pulp consume less oxidizing agent than the theoretical amount because they contain oxycelluloses. Therefore, a somewhat higher figure, 6,85 mg, is used in this method.

10.2 Accuracy of determination and expression of results

The results of two determinations should agree within 0,3 %.

Report the mean alkali solubility to one decimal place. Use symbols S_{10}, S_{18}, etc. corresponding respectively to concentrations of 10 g, 18 g, etc. of sodium hydroxide per 100 g of solution (see note 5 of clause 9).

NOTE – For pulps containing less than 0,1 % ash and other non-carbohydrate materials, the value $(100 - S_c)$ approaches the value R_c found by the method of determination of alkali resistance of pulp, described in ISO 699.

11 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

ANNEX

EXAMPLE OF CALCULATION

Mass of the air-dry test piece	1,735 g
Dry matter content determined on a separate sample	92,4 %
Mass of the test piece calculated on the basis of oven-dry pulps (m)	1,604 g
Volume of ammonium iron(II) sulphate solution consumed in the blank test (V_2)	41,1 ml
Volume of ammonium iron(II) sulphate solution consumed in the titration of the sample (V_1)	15,5 ml
Normality of ammonium iron(II) sulphate solution (N)	0,100 5
Volume of filtrate used in the oxidation (V)	10 ml

Solubility in sodium hydroxide solution (S_c) =

$$\frac{68{,}5\ (41{,}1 - 15{,}5)\ 0{,}100\ 5}{1{,}604 \times 10} = 11{,}0\ \%$$