International Standard

ISO 692

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.

International Standard ISO 692 was developed by Technical Committee ISO/TC 6, *Paper, board and pulps*.

This second edition was submitted directly to the ISO Council, in accordance with clause 6.11.2 of part 1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 692-1974), which had been approved by the member bodies of the following countries :

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

The member body of the following country had expressed disapproval of the document on technical grounds :

Netherlands

Pulps — Determination of alkali solubility

0 Introduction

The object of both this International Standard and 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 of the pulp and applies to all categories of pulps.

1 Scope and field of application

This International Standard specifies a method for the determination of the solubility of pulp in cold sodium hydroxide solutions of various and fixed concentrations. The sodium hydroxide concentrations most frequently used are 18 and 10 % (m/m).

The 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.

2 Reference

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

3 Definitions

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

3.2 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.

4 Principle

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

5 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

— 5,39 ± 0,03 mol/l solution, containing 18,0 ± 0,1 g of sodium hydroxide per 100 g of solution (ϱ_{20} = 1,197 2 g/ml), equivalent to 215,5 ± 1,0 g of sodium hydroxide per litre;

— 2,77 ± 0,03 mol/l solution, containing 10,0 ± 0,1 g of sodium hydroxide per 100 g of solution (ϱ_{20} = 1,108 9 g/ml), equivalent to 110,9 ± 1,0 g of sodium hydroxide per litre.

NOTE — The sodium hydroxide solution may be conveniently prepared as follows :

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

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

NOTE — If the concentration of the sulphuric acid is less than 94 % (V/V), the temperature will not reach the 125 to 130 °C required during the oxidation.

5.3 Potassium dichromate, about 0,067 mol/l solution in 2,7 mol/l sulphuric acid solution : 20 g of potassium dichromate ($K_2Cr_2O_7$) and 150 ml of sulphuric acid ($\varrho_{20} = 1,84$ g/ml) per litre of solution.

5.4 Ammonium iron(II) sulphate, approximately 0,1 mol/l solution (concentration known to an accuracy of $\pm$ 0,000 2 mol/l) : 40 to 41 g of ammonium iron(II) sulphate hexahydrate [$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$] and 10 ml of sulphuric acid ($\varrho_{20} = 1,84$ g/ml) per litre of solution.

This solution is not stable and its concentration shall be checked every day.

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

Prepare the reducing agent as follows :

Wash metallic cadmium (which passes a sieve of aperture size 1,4 to 2,0 mm, complying with the requirements of ISO 565) with water to remove fine particles. Treat the metal 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 wash the amalgamated metal.

The ammonium iron(II) sulphate solution may be standardized against potassium dichromate as a primary standard.

The concentration of the ammonium iron(II) sulphate solution will stay constant if 5 g of aluminium shavings, of purity greater than 99,99 %, are added to 10 l of solution.

5.5 Phosphoric acid, 85 % (V/V) ($\varrho_{20} = 1,70$ g/ml).

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

5.7 Sodium diphenylaminosulphonate indicator solution : dissolve 0,1 g of sodium diphenylaminosulphonate ($C_{12}H_{10}NSO_3Na$) in water and dilute to 100 ml.

6 Apparatus

Ordinary laboratory apparatus, and

6.1 Stirring equipment, with a propeller-type agitator made of stainless steel or other corrosion-resistant 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 15 W, operating at a rotational frequency between about 28 and 24 s^{-1}.

6.2 Constant temperature bath, capable of maintaining a temperature of 20 $\pm$ 0,2 °C.

6.3 Filter crucibles or **funnels,** of capacity 50 ml, made of alkali-resistant material, with a sintered glass disc of porosity grade P40 in accordance with ISO 4793.

6.4 Suction flasks, for the crucibles or funnels.

6.5 Balance, accurate to 1 mg.

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

Dimensions in millimetres
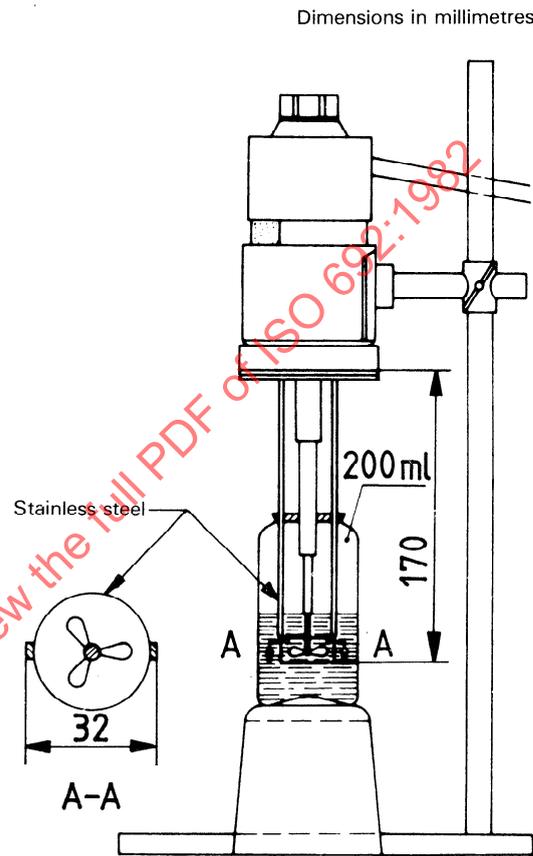
Figure

7 Preparation of the test sample

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

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,005 g, the equivalent amount of approximately 1,5 g of oven-dry pulp. Then immediately weigh two test portions for the determination of the dry matter content in accordance with ISO 638.

8.2 Determination

By means of a pipette, transfer 100,0 $\pm$ 0,2 ml of the chosen sodium hydroxide solution (5.1) to the reaction vessel (6.6).

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Adjust the temperature to 20 ± 0,2 °C (see note 1) by placing it in the constant temperature bath (6.2).

Add the test portion to the sodium hydroxide solution and allow 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 filter crucible or funnel[1] avoiding passage of air through the residue. Reject the first 10 to 20 ml and collect the next 40 to 50 ml of the filtrate in a clean bottle or flask.

By means of a pipette, transfer 10,0 ml (see note 3) of this filtrate to a 250 ml conical flask. Add, by means of a pipette, 10,0 ml of the potassium dichromate solution (5.3) and then carefully add, with swirling, 30 ml of the concentrated sulphuric acid (5.2). Check that the temperature is between 125 and 130 °C.

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

According to the case, proceed as follows :

a) To the cold solution, add 50 ml of water. Cool again, add 2 drops of the ferroin indicator solution (5.6) and titrate with the freshly standardized (see the note to 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 (5.5). Cool again, and titrate rapidly with the freshly standardized ammonium iron(II) sulphate solution (5.4) until about 90 % of the required amount has been added. Then, by means of a pipette, add 1 ml of the sodium diphenylaminosulphonate indicator solution (5.7), and titrate further without delay to the colour change from dark brown through violet to bright green (see note 4).

Carry out 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 18 % (m/m) 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 sodium hydroxide solution of lower concentration [for example 10 % (m/m)] is much more dependent on temperature. At this lower concentration, the temperature 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 test portion 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 % (m/m), reduce the volume of the aliquot portion to 5 ml and the amount of sulphuric acid to 25 ml. If the alkali solubility is less than 5 % (m/m), 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 to be negligible.

5 Alternatively, an iodometric titration procedure can be used, but its use shall be stated in the test report.

Transfer the cold solution, after oxidation, to a 1 000 ml conical flask, using 500 ml of 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 mol/l sodium thiosulphate solution ($Na_2S_2O_3$), adding powdered starch indicator when the yellow colour of the iodine has nearly disappeared. The end point is indicated by a change from deep blue to light green. Carry out a blank test, substituting a 10 ml portion of the sodium hydroxide solution for the filtrate. Calculate the result as described in 9.1, substituting for V_1 and V_2 the corresponding volumes of sodium thiosulphate solution and for c the concentration of the solution.

9 Expression of results

9.1 Method of calculation and formula[2]

The alkali solubility, S_c, expressed as a percentage by mass, is given by the formula

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

where

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

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

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

2) An example of the calculation is given in the annex.

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

c is the concentration, in moles per litre, of the ammonium iron(II) sulphate solution;

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

6,85 is the empirical factor, in milligrams, indicating the amount of cellulose equivalent to 1/6 mmol of potassium dichromate.

NOTE — Theoretically, 1/6 mmol 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.

9.2 Precision and expression of results

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

Report the mean alkali solubility to one decimal place, using the symbols S_{10}, S_{18}, etc.

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

10 Test report

The test report shall include the following particulars :

a) a reference to this International Standard;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

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

Annex

Example of calculation

Mass of the air-dry test portion	1,735 g
Dry matter content determined on a separate test portion	92,4 %
Mass of the test portion calculated on the oven-dry basis (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 test portion (V_1)	15,5 ml
Concentration of the ammonium iron(II) sulphate solution (c)	0,100 5 mol/l
Volume of filtrate used in the oxidation (V)	10 ml

Solubility in sodium hydroxide solution (S_c) =

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

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