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APPENDIX A

JAPANESE INDUSTRIAL STANDARD

JIS K 0070 - 1966

A.1 Scope

This standard specifies testing methods for acid value, iodine value and hydroxy value of chemical products.

A.2 Method of Test

A.2.1 Acid Value The acid value is defined by the number of milligrams of potassium hydroxide required to neutralize free fatty acids contained in 1 g of the sample.

A.2.1.1 Reagents

(a) Solvents A(1 + 1) or (2 + 1) mixture of ethyl ester and ethyl alcohol or a (1 + 1) or (2 + 1) mixture of benzene and ethyl alcohol shall be used. These mixtures shall previously be neutralized prior to use with N/10 ethyl alcoholic potassium hydroxide solution using phenolphthalein as the indicator.

(b) Phenolphthalein Solution: Dissolve 1 g of phenolphthalein in 100 ml of ethyl alcohol (95 v/v %).

(c) N/10 ethyl alcoholic potassium

hydroxide solution: Dissolve 7.0 g of potassium hydroxide in minimum amount of water and dilute with ethyl alcohol (95 v/v%) to 1000 ml. After standing for 2 to 3 days, filter and standardize in accordance with 2.(10) or 2.(11) of JIS K 8006-Fundamental Articles on Volumetric Determinations.

A.2.1.2 Procedure Weigh accurately proper amount (*) of the sample and add 100 ml of the solvent and few drops of phenolphthalein indicator solution. Vigorously shake until the sample is dissolved completely. For solid sample, it shall be heated on a water bath until the sample is dissolved completely. After cooling, titrate with N/10 ethyl alcoholic potassium hydroxide solution until a pale pink colour persists for 30 seconds.

Notes (*) The amount of the sample to be taken shall be as directed below.

Expected acid value	Weight of sample to be taken (g)
less than 5	20 (to 2 significant digits)
5 to 15 excl.	10.0 (to 3 significant digits)
15 to 30 excl.	5.00 (to 3 significant digits)
30 to 100 excl.	2.00 (to 3 significant digits)
100 and over (#).	1.000 (to 4 significant digits)

(#) For samples having acid value 100 and over, the titration shall be made with N/2 ethyl alcoholic potassium hydroxide solution.

A.2.1.3 Calculate the Acid Value, A, by the following formula:

$$A = \frac{B \times f \times 5.611}{S}$$

B: volume of N/10 ethyl alcoholic potassium hydroxide solution consumed in titration (ml)

f: factor of N/10 ethyl alcoholic potassium hydroxide solution

S: weight of sample (g)

Remarks

1. If the sample is imparted with dark colour, the following precautions shall be exercised.

(a) Alkali blue 6 B or thymolphthalein shall be used as the indicator.

(b) Phenolphthalein test paper shall be used as the external indicator.

(c) An Erlenmeyer flask provides with side tube shall be used for determining end point as revealed by the colour change of the solution in the side tube.

(d) The titration shall be made with alkaline solution of high concentration.

(e) The sample shall be taken in minimum amount and the considerable amount of the solvent shall be used.

(f) Dissolve the sample in the solvent and add saturated sodium chloride solution. Titrate with alcoholic potassium hydroxide solution using phenolphthalein indicator solution until the sodium chloride solution layer is imparted with pink colour.

A.2.2 Iodine Value The iodine value is defined by the amount of halogen (calculated to the number of grams of iodine) absorbed by 100 g of the sample under the prescribed conditions.

A.2.2.1 Reagents

(a) Wijs' solution, prepared alternatively by Method A or Method B as described below.

Wijs' solution is more stable if iodine is continued in slightly excess and it often gives high result of iodine value if chlorine is contained in excess. This solution shall be stored in a brown bottle, or in a dark place. When it might freeze in winter, it shall be heated to a temperature not higher than 40°C prior to use.

Method A : Dissolve 13 g of iodine in 1000 ml of acetic acid. Pipette 20 ml of the solution and titrate with N/10 sodium thiosulfate solution to determine the concentration of iodine. After dried chlorine is introduced in the solution, pipette 20 ml of the solution, add 15 ml of potassium iodide solution (10 w/v %) and 100 ml of water, and titrate with

N/10 sodium thiosulfate solution so that the titre measures twice the initial titre. The titration shall be made after chlorine gas is introduced in the solution until the colour of liberated iodine disappears, reserving small portions of the solution aside before introducing chlorine. If chlorine is present excessively, it shall be removed by adding appropriate amount of iodine solution reserved.

Method B : Weigh 7.9 g of iodine trichloride and 8.7 g of iodine into separate flasks. Dissolve them in acetic acid, mix well and dilute with acetic acid to 1000 ml .

(b) Potassium iodide solution (10 w/v %) :
Dissolve 100 g of potassium iodide in 1000 ml of water.

(c) N/10 Sodium thiosulfate solution :
Dissolve 24.8 g of sodium thiosulfate in water and dilute it with water to 1000 ml . This solution shall be standardized as follows.

Standardization Take 10 ml of potassium iodide solution (w/v %) into a glass-stoppered Erlenmeyer flask and add 5 ml of hydrochloric acid and shake well. Add exactly 25 ml of N/10 potassium dichromate solution (primary standard substance), tightly stopper with a glass stopper wet with potassium iodide solution (10 w/v %) and gently shake the flask. Add 100 ml of water, shake and titrate with N/10 sodium thiosulfate solution until the yellow colour almost disappears. Add 1 ml of starch solution and continue the titration until the blue colour of iodine-starch changes to green.

Run the blank titration and calculate the factor of N/10 sodium thiosulfate solution, f , by the following formula :

$$f = \frac{25}{A - B}$$

A: volume of N/10 sodium thiosulfate solution consumed in actual titration (ml)

B: volume of N/10 sodium thiosulfate solution consumed in blank titration (ml)

(d) Starch solution : Tritrate 1 g of soluble starch with small amount of water and pour slowly, with constant stirring, into 200 ml of boiling water. Cool it down to room temperature and the supernatant liquid or the filtrate shall be used for test.

(e) N/10 Potassium dichromate solution (primary standard substance) : Pulverize potassium dichromate specified in JIS K 8005 and heat at 100 to 110 C for 3 to 4 hours. Dissolve 4.9035 g (on the basis of 100 %) of this reagent in water. Transfer the solution to a 1000 ml volumetric flask and dilute with water to the mark.

A.2.2.2 Procedure Weigh accurately proper amount (&) of the sample into a ground-stoppered 500 ml Erlenmeyer flask and add 10 ml of carbon tetrachloride to dissolve the sample. Add exactly 25 ml of Wijs' solution and tightly stopper with a glass stopper wet with potassium iodide solution (10 w/v %) in order to prevent volatilization of iodine and chlorine and gently swirl the flask. If the clear solution is not obtained, carbon tetrachloride shall be added additionally until the solution becomes clear. Place the flask in a dark place kept at a temperature of 20 to 30 C for proper period (30 minutes for the sample having iodine value not

more than 100, 1 hour for iodine value 100 and over, and 2 hours for tung oil) and swirl the flask occasionally. Add 20 ml of potassium iodine solution (10 w/v %) and 100 ml of water, swirl the flask and titrate with N/10 solution until the solution colours pale yellow. Add 1 ml of starch solution and continue the titration, with swirling, until the blue colour of iodine-starch disappears.

Run the blank titration.

Note (&) The sample shall be taken as directed below in such amount that not more than one half of Wijs' solution is consumed.

Expected iodine value	Weight of sample to be taken (g)
less than 5	2.00 (to 2 significant digits)
5 to 30 excl.	1.00 (to 3 significant digits)
30 to 50 excl.	0.60 (to 3 significant digits)
50 to 100 excl.	0.30 (to 3 significant digits)
100 to 150 excl.	0.20 (to 3 significant digits)
150 to 200 excl.	0.150 (to 4 significant digits)
200 and over	0.100 (to 4 significant digits)

A.2.2.3 Calculate iodine value, A, by the following formula :

$$A = \frac{(B - C) \times f \times 1.269}{S}$$

B: volume of N/10 sodium thiosulfate solution consumed in blank titration(ml)

C: volume of N/10 sodium thiosulfate solution consumed in actual titration (ml)

f: factor of N/10 sodium thiosulfate solution

S: weight of sample(g)

A.2.3 Hydroxyl Value The hydroxyl value is defined by the number of milligrams of potassium hydroxide required to neutralize acetic acid which has been combined with hydroxyl radical when 1 g of the sample is acetylated by a specified procedure.

A.2.3.1 Reagents

(a) Acetylation Reagent Weigh 25g of acetic anhydride into a 100 ml volumetric flask, add pyridine to the mark and shake vigorously. This solution shall be stored tightly in a brown protected from atmospheric moisture, carbon dioxide and acid vapours.

(b) Phenolphthalein solution : Dissolve 1 g of phenolphthalein in 100 ml of ethyl alcohol (95 v/v %).

(c) N/2 ethyl alcoholic potassium hydroxide solution : Dissolve 35 g of potassium hydroxide in minimum amount of water and dilute with ethyl alcohol (95 v/v %) to 1000 ml. Stand for 2 to 3 days and filter. Standardize this solution in accordance with 2. (11) of JIS K 8006.

A.2.3.2 Procedure Weigh accurately proper amount (*) of the sample into a round-bottomed flask and add 5 ml of acetylation reagent. Place a small funnel on the mouth of the flask and immerse in a glycerine bath kept a temperature of 95 to 100 C so deep that the bottom of the flask is approximately 1 cm below the bath liquid. A piece of circular pressboard pierced with a round hole shall be placed over the sphere of the flask to protect the neck of the flask against the heat from the bath. After heating for 1 hour, take the flask out of the bath and allow to cool. Add 1 ml of water through the funnel and swirl the flask to decompose acetic anhydride. Reheat the flask in the glycerine bath for 10 minutes to complete the decomposition and allow to cool. Wash the funnel and the inside of the flask with 5 ml of ethyl alcohol and titrate with N/2 ethyl alcoholic potassium hydroxide solution using phenolphthalein solution as the indicator.

Run the blank titration.

Note (*) The amount of the sample to be taken shall be as directed below depending on the hydroxyl value of the sample

Where the sample has hydroxyl value 10 or less, the amount of the sample shall be increased, and minimum amount of pyridene shall be added additionally to dissolve the sample if it is hardly soluble in acetylation reagent.

Where the sample has hydroxyl value exceeding 500, the amount of the sample be diminished in a proportion given above.

Hydroxyl value	Weight of sample to be taken
10 to 100 excl.	2.00 (to 3 significant digits)
100 to 150 excl.	1.50 (to 3 significant digits)
150 to 200 excl.	1.00 (to 3 significant digits)
200 to 250 excl.	0.75 (to 3 significant digits)
250 to 350 excl.	0.70 (to 3 significant digits)
350 to 500 excl.	0.50 (to 3 significant digits)

A.2.3.3 Calculate the hydroxyl value, A, by the following formula:

$$A = \frac{(B - C) \times f \times 28.05}{S} + D$$

B: volume of N/2 ethyl alcoholic potassium hydroxide solution consumed in blank titration (ml)

C: volume of N/2 ethyl alcoholic potassium hydroxide solution consumed in actual titration (ml)

f: factor of N/2 ethyl alcoholic potassium hydroxide solution

S: weight of sample (g)

D: acid value

Remarks

1. This method is not applicable to tertiary alcohol as lower result may be caused.

2. The test results may vary in wide range if aldehydes are contained in the sample.

3. Alkali blue 6 B solution is recommended as the indicator when the solution colours deep on titration.

APPENDIX B

H₂ ADSORPTION AND BET MEASUREMENT

B.1 H₂ Adsorption Measurement.

About 0.05 g of catalyst was weighed and packed in a quartz tube of 0.52 cm I.D. The catalyst was heated up to 400°C in the atmosphere of hydrogen and held at this temperature for 10 minutes. Then the catalyst was cooled down to room temperature. The flow of nitrogen gas at the rate of 30 cc/min was subsequently introduced into the tube through the bed of the catalyst. At room temperature 2 cc of H₂ was injected into the tube passing through the catalyst. The amount of H₂ adsorbed onto the catalyst was then determined.

The amounts of H₂ adsorbed for the Raney nickel and Raney nickel incorporated with palladium compound were shown in Table B.1.

Table B.1. H₂ Adsorption for Raney Nickel and Raney Nickel Incorporated with Palladium Compound.

Type of catalyst	H ₂ adsorped (cc/g-catalyst)
Raney nickel	2.2356
Pd1	2.3817
Pd2	1.9487
Pd3	2.3923
Pd4	1.6268

B.2 Measurement of Surface Area using BET Analyzer.

The Raney nickel and Raney nickel incorporated with palladium compound were characterized using BET analyzer to determine total surface area. The results were shown in Table B.2.

Table B.2. Total Surface Areas of Raney Nickel and Raney Nickel Incorporated with Palladium Compound.

Type of catalyst	Total surface area (m^2/g)
Raney nickel	3.60
Pd1	10.03
Pd2	6.82
Pd3	7.67
Pd4	3.47

VITA

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