

JIS

JAPANESE INDUSTRIAL STANDARD

**Testing Methods for
Synthetic Detergent**

JIS K 3362—1990

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In the event of any doubt arising,
the original Standard in Japanese is to be final authority.

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JAPANESE INDUSTRIAL STANDARD
Testing Methods for Synthetic Detergent

J I S
K 3362-1990

1. Scope

This Japanese Industrial Standard specifies the testing methods for household synthetic detergents.

Remark: In this Standard the units and numerical values shown in { } are in accordance with the traditional units and are standard values.

2. Common Matters

2.1 Definitions For the purposes of this Standard the main definitions are in accordance with JIS K 3211.

2.2 General Matters General matters common to the test are in accordance with JIS K 0050.

3. Test Items

Test items specified in this Standard are divided into sampling methods, chemical tests, physical tests and detergency evaluation methods and are as follows:

3.1 Sampling Method

3.2 Chemical Tests

- (a) Determination of Petroleum Ether Soluble Matter
- (b) Ethanol Soluble Matter
- (c) Qualitative Test and Determination of Anionic Surface Active Agent
- (d) Qualitative Test and Determination of Cationic Surface Active Agent
- (e) Qualitative Test and Determination of Nonionic Surface Active Agent
- (f) Determination of Urea
- (g) Determination of Equivalent to Surface Active
- (h) Determination of Sodium Carboxymethylcellulose
- (i) Determination of Peroxide
- (j) Determination of Total Phosphate
- (k) Determination of Silicate
- (l) Determination of Sulfate
- (m) Determination of Carbonate
- (n) Determination of Chloride
- (o) Determination of Zeolite
- (p) Confirmation Test of Fluorescent Brightener
- (q) Limit Test of Arsenic (As)
- (r) Limit Test of Heavy Metal (As Pb)
- (s) Determination of Methanol
- (t) Determination of Ethanol
- (u) Determination of Moisture

Applicable Standards, Corresponding International Standards: See pages 69 to 71.

3.3 Physical Tests

- (a) Grain Size
- (b) Apparent Density
- (c) pH Value
- (d) Surface Tensile Strength
- (e) Foaming Power and Stability of Foam
- (f) Stability in Hard Water

3.4 Detergency Evaluation Methods

- (a) Detergency Evaluation Method for Synthetic Detergent for Cloth
- (b) Detergency Evaluation Method for Synthetic Detergent for Kitchen

4. Sampling Method

4.1 Sampling of Representative Sample Form a lot considered to be the same quality such as products manufactured in the same lot, products made within a definite time after continuous manufacturing in the same facility, and the like, corresponding to the number of containers of the lot, take the representative sample of the specified quantity of the number of pieces shown in Table 1 at random according to the suitable method such as random table. However, in case where the containers exceed 1000 pieces, even to its fraction, apply Table 1.

Table 1. Taking Number of Samples

Number of containers	Number of sampling
1 to 10	1
11 to 50	2
51 to 100	3
101 to 500	5
501 to 1000	10

Remark: Relating to the number of sampling, it may be determined according to the process capacity.

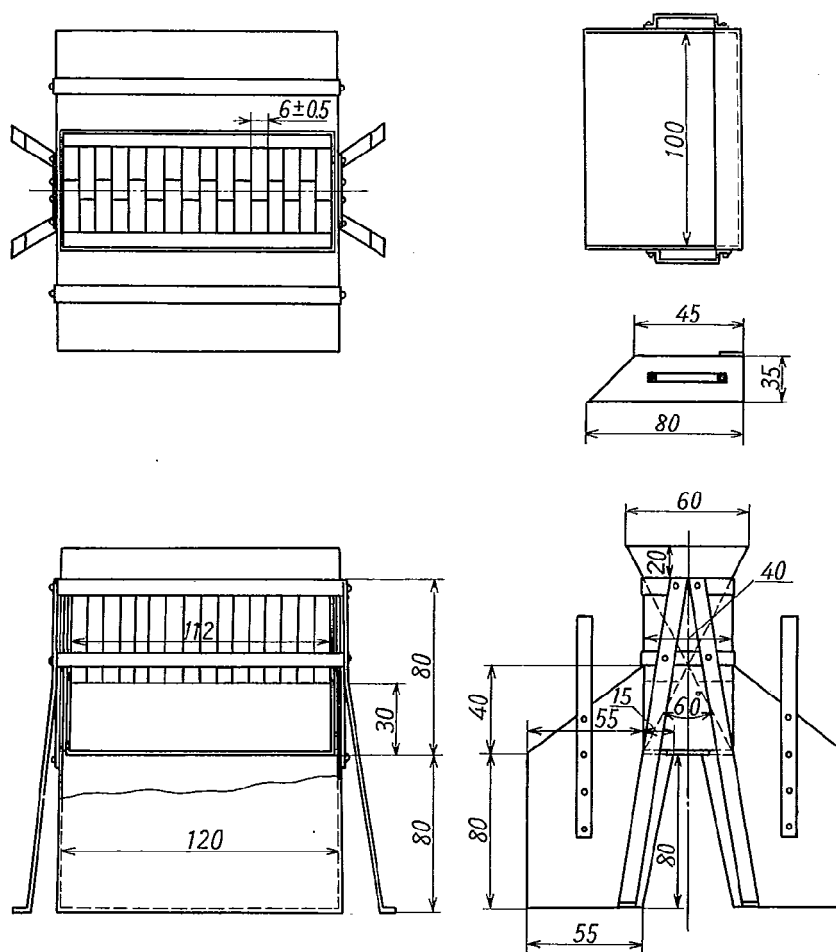
4.2 Preparation of Sample Mix the representative samples taken according to 4.1 and according to the profile of products prepare the samples.

4.2.1 Apparatus The apparatus shall be as follows.

- (1) Reduction Apparatus The reduction apparatus of No. 6 of Attached Fig. 4 of JIS M 8100. An example is shown in Fig. 1.
- (2) Beaker A beaker made of glass or stainless steel, of 1 l in capacity.

Fig. 1. An Example of Reduction Apparatus

Unit: mm



4.2.2 Operation The operation shall be carried out as follows:

- (1) **Pulverized State or Grain State Sample** With taking so care to the representative sample taken in 4.1 as not to break particle itself, loosen the grain having become a specially large lump to mix, apply the total amount to a reduction apparatus and repeat until a suitable quantity sample to be used for test is obtained.

- Remarks 1. At the time of using a reduction apparatus, care shall be taken to clogging, shaking method of sample container. In the case of carrying out the repeating operation, if take matters at only one side of reduction apparatus, there is a fear to generate bias, and therefore which is taken shall be selected at random.
2. The pulver state or grain state detergent may have nonuniform property and it is, in some cases, difficult to take representative sample. Particularly the pulver state detergent which is added with other materials after receiving spray, dry and cooling process is physically mixing, therefore each component is in inclination to be separated only by vibration, and therefore it is necessary to apply the total of taken representative sample to reduction apparatus.

- (2) Liquid State or Pasty State Sample Transfer the representative sample taken in 4.1 to a beaker, and mix. When the liquid or paste is transparent and uniform, take separately a suitable amount from this and take it as the sample.

In this case, when it is opaque and contains precipitate, while taking so care the air bubbles not to enter, mix by stirring with a glass rod, and if required warm it in water bath at 50 to 60°C⁽¹⁾(²). After becoming uniform, while mixing by stirring cool until 15 to 30°C, and take separately a suitable amount to take it as the sample. Enter this sample in a glass bottle or polyethylene bottle with ground-in stopper, and store in a cool, dark place.

Notes ⁽¹⁾ Products on the market may have pH value of 6.5 or under and, be unsuitable to heat to 50 to 60°C and therefore cares shall be taken to handling.

⁽²⁾ In the case of heating, the loss due to evaporation of water shall be taken into consideration, and therefore the mass shall be measured before and after heating.

5. Chemical Tests

5.1 Determination of Petroleum Ether Soluble Matter

5.1.1 Summary As to the petroleum ether soluble matter, in the case where the water-ethanol solution of sample is extracted with petroleum ether, the amount to be solved in petroleum ether is obtained⁽³⁾.

Note ⁽³⁾ Among the nonionic surface active agents, there are those to be extracted in petroleum ether.

5.1.2 Reagents Reagents shall be as follows:

- (1) Petroleum Ether The petroleum ether specified in JIS K 8593, distilled at 30 to 60°C.
- (2) Mixed Solution of Water-Ethanol The mixture of ethanol specified in JIS K 8102 with water in equal amount.
- (3) Sodium Sulfate (Anhydride) The sodium sulfate specified in JIS K 8987.
- (4) 0.5 mol/l (N/2) Sodium Hydroxide Solution The 0.5 mol/l (N/2) sodium hydroxide solution specified in 4.4 (20.2) of JIS K 8001.
- (5) Phenolphthalein Solution (1 w/v %) The phenolphthalein 1 g specified in JIS K 8799 dissolved in ethanol (95) 100 ml.

5.1.3 Operation The operation shall be carried out as follows:

- (1) Weigh out the sample approximately 10 g into an Erlenmeyer flask of 300 ml to the nearest 1 mg and dissolve in water-ethanol mixed solution 200 ml. If there are insolubles at this time, filter them.
- (2) Add 0.5 mol/l (N/2) sodium hydroxide solution 5 ml, and drop phenolphthalein solution (1 w/v %) to confirm that it is alkaline.
- (3) Transfer to a separatory funnel of 500 ml, and extract three times by each petroleum ether 50 ml. When the emulsion is generated, add a small amount of ethanol to extinguish.
- (4) Join the petroleum ether layer, wash three times with water-ethanol mixed solution of each 30 ml and wash two times with water of each 30 ml, after dehydration with sodium sulfate (anhydride), filter by using dried filter paper into an Erlenmeyer flask of 300 ml of known mass, and wash the filter paper with a small amount of petroleum ether.
- (5) Vaporize the petroleum ether on water bath, leave the Erlenmeyer flask in a desiccator to cool until room temperature, feed dry air to inside of Erlenmeyer flask and

after expelling until the odor of remaining petroleum ether extinguishes, weigh the mass.

Remark: Join the residual solution of petroleum ether extraction and washings to preserve and use for 5.3.3 Determination of Soap Content.

5.1.4 Calculation Calculate the petroleum ether solubles according to the following formula.

$$C = \frac{A}{S} \times 100$$

where, C : petroleum ether solubles (%)
 A : petroleum ether extraction amount (g)
 S : mass of sample (g).

5.2 Determination of Ethanol Solubles

5.2.1 Summary As to ethanol solubles, the sample is dissolved by ethanol and the mass of substances soluble in ethanol when extracted is obtained.

5.2.2 Reagents Reagents shall be as follows:

- (1) Ethanol (95) Ethanol specified in JIS K 8102.
- (2) Ethanol (99.5) Ethanol specified in JIS K 8101.

5.2.3 Apparatus The apparatus shall be as follows.

- (1) Erlenmeyer Flask An Erlenmeyer flask of 300 ml attached with a glass tube of 65 cm or more in length.
- (2) Glass Filter The filter plate of fine aperture symbol 4 specified in JIS R 3503.
- (3) Receiver for Filtration
- (4) The dryer capable of adjusting at $105 \pm 2^\circ\text{C}$.

5.2.4 Operation The operation shall be carried out as follows:

- (1) Weigh out the sample approximately 5 g into an Erlenmeyer flask 300 ml to the nearest 1 mg, add ethanol⁽⁴⁾ 100 ml, attach a glass tube and while mixing by shaking at times on the water bath for 30 min to dissolve.
- (2) Filter the warm solution as it is by using a glass filter, and add again ethanol (95) 50 ml to the residual of Erlenmeyer flask to dissolve. Filter the warm solution by using a glass filter, and wash thoroughly the Erlenmeyer flask and glass filter with hot ethanol. Leave to cool to room temperature, transfer the filtrate and washings to one mark volumetric flask 250 ml, and add ethanol (95) up to the marked line. From this, separately take each 100 ml into two beakers of 200 ml of known mass by using a transfer pipet.
- (3) Heat the one piece out of them on water bath, after removing ethanol, dry in an oven adjusted at $105 \pm 2^\circ\text{C}$ for 1 h and after leaving to cool in a desiccator, measure the mass.

Note ⁽⁴⁾ For pulver state or grain state sample use ethanol (95) and for liquid state or paste state sample use ethanol (99.5).

5.2.5 Calculation Calculate the soluble content of ethanol according to the following formula:

$$C = \frac{A}{S \times \frac{100}{250}} \times 100 = \frac{250 \times A}{S}$$

where, C : ethanol soluble content (%)
 A : residual amount of drying (g)
 S : mass of sample (g).

Remark: The residue on glass filter shall be the sample when determination of sodium carboxymethylcellulose of 5.8.1 and when determination of total phosphate of 5.10 and one piece of separately taken beaker shall be the sample when determination of nonionic surface active agent according to ion exchange chromatography shown in 5.5.3.1

In the case of carrying out the infrared absorption spectral analysis of surface active agent component, the ethanol soluble content used for determination shall be taken as sample.

5.3 Quality Test and Determination of Anionic Surface Active Agent

5.3.1 Quality Test of Anionic Surface Active Agent

- (1) **Summary** According to Operation I the anionic surface active agent other than soap generates the complex of Methylene Blue and blue, and the soap is detected by liberating the fatty acid by acidic solution according to Operation II.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Methylene Blue Solution** Add gradually the sulfuric acid 12 g specified in JIS K 8951 to water of 500 ml and cool. Dissolve the Methylene Blue 0.03 g specified in JIS K 8897 and sodium sulfate (anhydride) 50 g specified in JIS K 8987 into this, and add water to make 1 l.
 - (b) **Chloroform** Wash the chloroform specified in JIS K 8322 with Methylene Blue Solution (1 w/v %), add calcium oxide specified in JIS K 8410 or calcium chloride specified in JIS K 8123 to distill and by using sodium sulfate (anhydride) specified in JIS K 8987 dehydrate. Use it within three days after distillation.
 - (c) **Sulfuric Acid (50 v/v %)** The sulfuric acid (50 v/v %) prepared by using sulfuric acid specified in JIS K 8951.
- (3) **Operation I** The operation shall be carried out as follows:
 - (a) Put Methylene Blue solution approximately 5 ml and chloroform approximately 5 ml into a test tube, stopper to shake vigorously and stand still to separate layer⁽⁵⁾.
 - (b) Add to this one drop of approximately 1 w/v % (or 1 v/v %) solution of sample, after shaking up and down vigorously, stand still to separate layer, and if the chloroform layer becomes blue, it indicates the existence of anionic surface active agent⁽⁶⁾.
 - (c) Further, add sample solution, and when operated similarly, the chloroform layer becomes more dense blue.

Notes ⁽⁵⁾ The chloroform layer is ordinarily colorless but according to existence of impurities of Methylene Blue or of ethanol may become slight blue in some cases.

- (⁶) The coexistence of nonionic surface active agent, according to more or less emulsification phenomenon may require more time for layer separation, but it does not become interference to quality test.

(4) Operation II The operation II shall be carried out as follows:

- (a) Put approximately 1 w/v % (or 1 v/v %) solution of sample of approximately 5 ml into a test tube.
- (b) Add two to three drops of sulfuric acid (50 v/v %) to this, mix by shaking, make acidic at 4 or less pH value and stand still.
- (c) At this time, when the sample solution becomes white turbid according to liberation of fatty acid and separate gradually the oil state, it indicates the existence of soap. When the amount of soap is small, the detection by separating quantitatively according to 5.3.3 shall be carried out.

5.3.2 Determination of Anionic Surface Active Agent

- (1) Summary The long chain sulfonate such as alkylbenzenesulfonate, alkylsulfate, alkylethoxy sulfate, alkenyl sulfonate, alkyl sulfonate or sulfate forms complex compound with Methylene Blue and is dissolved in chloroform to become blue. When adding to this a sufficient amount of cationic surface active agent, the complex salt of anionic surface active agent and cationic surface active agent is generated, the Methylene Blue is liberated and so the anionic surface active agent can be determined.
- (2) Reagents Reagents shall be as follows.
 - (a) Anionic Surface Active Agent Standard Solution (0.004 mol/l (N/250)) Weigh out sodium lauryl sulfate on the market of approximately 1.2 g in pure content conversion to the nearest 0.1 mg, after dissolving in water, transfer into a one mark volumetric flask 1000 ml, and add water up to the marked line. Calculate the factor according to the following formula:

$$f_a = \frac{S \times \frac{P}{100}}{M \times \frac{1}{250}} = \frac{2.5 SP}{M}$$

where, f_a : factor

S : mass of sodium lauryl sulfate (g)

P : purity (%)

M : chemical formula weight of sodium lauryl sulfate.

Remark: Obtaining Method of Purity (P) and Chemical Formula Weight (M) of Sodium Lauryl Sulfate

The value of P shall be obtained according to the following:

Weigh out the refined sodium lauryl sulfate approximately 5 g according to recrystallization into an Erlenmeyer flask of 300 ml to the nearest 0.1 mg, add to this 0.5 mol/l (1 N) sulfuric acid 25 ml prepared by using sulfuric acid specified in JIS K 8951 by using a transfer pipet, attach a condenser and reflux by hot plate or on sand bath. Taking care to framing, with shaking slightly the Erlenmeyer flask at times reflux it, and after the solution has become transparent and not to foam, further reflux for 2 h. After cooling, wash the inner wall of condenser by using ethanol (99.5) of 5.2.2 (2) of 30 ml, and then after washing with a suitable amount of water, detach the condenser. After making approximately 100 ml the liquid amount by adding water, add several drops of phenolphthalein solution (1 w/v %), and titrate by 1 mol/l (1 N) sodium hydroxide solution prepared by sodium hydroxide

specified in JIS K 8576. At the same time carry out the blank test, and calculate the purity of sodium lauryl sulfate according to the following formula:

$$P = \frac{(A-B) \times f \times M}{S \times 1000} \times 100$$

where, P : purity (%)

A : amount of 1 mol/l (1 N) sodium hydroxide solution used for titration of sample (ml)

B : amount of 1 mol/l (1 N) sodium hydroxide solution used for titration of blank test (ml)

f : factor of 1 mol/l (1 N) sodium hydroxide solution

M : chemical formula weight of sodium lauryl sulfate

S : mass of sample (g).

The value of M shall be obtained according to the following:

Take the phenolphthalein solution (1 w/v %) of remark to obtain the above-mentioned P as the indicator, transfer 50 ml of the titration solution after titrating with 1 mol/l (1 N) sodium hydroxide solution to a 300 ml separatory funnel, add 100 ml of ethanol (99.5) (2 + 1) prepared with ethanol (99.5) specified in JIS K 8101, and extract twice with each 50 ml of petroleum ether specified in JIS K 8593. Join the petroleum ether layer, wash with water of each 50 ml twice, and after dehydrating with sodium sulfate (anhydride) specified in JIS K 8987, concentrate to a suitable concentration to measure the distribution of number of carbons according to gas chromatograph analysis. Carry out the gas chromatograph analysis according to JIS K 0114 under the most suitable measuring conditions, obtain percentage of each component of sample alcohol, obtain the average molecular weight of sample alcohol, and from this obtain the chemical formula weight M of sodium lauryl sulfate.

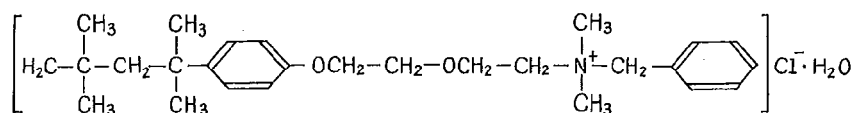
Informative Reference: For stationary phase liquid, use chromosolve W with 10 % of silicone SE-30, carry out with column tank temperature of 180°C, for carrier gas using nitrogen or helium, for detector the hydrogen flame ionization detector at thermostatic temperature.

- (b) Cationic Surface Active Agent Standard Solution (0.004 mol/l Benzethonium Chloride Solution) The preparation and standardization shall be carried out as follows.

Preparation Dissolve approximately 1.9 g of benzethonium chloride (monohydrate) on the market in water to make 1 l, and take it as the cationic surface active agent standard solution.

This standard solution 20 ml consumes anionic surface active agent standard solution 20 ml in the blank test of following (4).

Informative Reference: Benzethonium Chloride (Monohydrate) is shown in its structure as follows. On the market, there exists Hyamine 1622 (Rohm & Haas Corp.).



Standardization Take anionic surface active agent standard solution (0.004 mol/l) 10 ml into a cylinder for titration, add Methylene Blue solution 25 ml and chloroform 15 ml, and then after adding water of 20 ml, titrate with cationic surface active agent standard solution. For titration at first each 2 ml, at each time stopper, and after shaking vigorously stand still. When the separation of two layers is quick, reduce sequentially the titration amount, and at near the end point carry out at each one drop (0.02 to 0.03 ml), let a white plate be background and take the time when the blue of both layers has become the same as the end point. Calculate the factor of cationic surface active agent standard solution according to the following formula.

$$f_c = \frac{10 \times f_a}{A}$$

where, f_c : factor of cationic surface active agent standard solution
 A : amount of cationic surface active agent standard solution used for titration (ml)
 f_a : factor of anionic surface active agent standard solution.

In the case of applying the back titration method (A method) of (4) (4.1.1), the standardization of factor of cationic surface active agent standard solution is not required.

- (c) **Methylene Blue Solution** The Methylene Blue solution is in accordance with 5.3.2 (2) (a).
- (d) **Chloroform** The chloroform is in accordance with 5.3.2 (2) (b).
- (e) **Phenolphthalein Solution (1 w/v %)** The phenolphthalein solution is in accordance with 5.1.2 (5).
- (f) **0.5 mol/l (1 N) Sulfuric Acid** The 0.5 mol/l (1 N) sulfuric acid specified in 4.4 (28) of JIS K 8001.
- (g) **2 mol/l (2 N) Sodium Hydroxide Solution** Add water to sodium hydroxide approximately 83 g specified in JIS K 8576 to dissolve and make 1 l.
- (3) **Apparatus** Cylinder for titration The measuring cylinder having stopper of 100 ml 1 type specified in JIS R 3505.
- (4) **Operation** The operation shall be carried out as follows:
 - (4.1) **Determination of Bond Sulfuric Acid of Total Anionic Surface Active Agent**
 - (4.1.1) **Back-titration Method (Method A)**
 - (a) Weight out a suitable amount (including approximately 1.4 g as pure content) of sample to the nearest 0.1 mg, add water 200 ml to dissolve by heating, after cooling, transfer to one mark volumetric flask 1000 ml, add water to make 1 l and take it as sample solution.
 - (b) From this, take 10 ml into a cylinder for titration, add Methylene Blue solution 25 ml and chloroform 15 ml, and add cationic surface active agent standard solution [0.004 mol/l (N/250)] 20 ml by means of a transfer pipet.
 - (c) At first add each 2 ml of anionic surface active agent standard solution, stopper at each time and after shaking vigorously, stand still. When the separation of two layers becomes quick, reduce sequentially the titration amount, at near the end point carry out at each one drop, take a white plate as the background and take the time when the blue of both layers has become the same as the end point.

- (d) At the same time carry out the blank test.
- (e) Calculation Calculate the bond sulfuric acid of total anionic surface active agent according to the following formula.

$$C = \frac{(B-A) \times \frac{1}{250} \times f_a \times 80.06}{S \times 1000 \times \frac{10}{1000}} \times 100 = \frac{3.20 (B-A) \times f_a}{S}$$

where, C : bond sulfuric acid of total anionic surface active agent (as SO_3) (%)

B : amount of anionic surface active agent standard solution used for titration of blank test (ml)

A : amount of anionic surface active agent standard solution used for titration of sample solution (ml)

f_a : factor of anionic surface active agent standard solution

S : mass of sample (g)

80.06 : chemical formula weight of SO_3 .

(4.1.2) Direct Titration Method (Method B)

- (a) Take the sample solution 10 ml of 4.1.1 (a) into a cylinder for titration, and add Methylene Blue solution 25 ml, chloroform 15 ml and water 20 ml.
- (b) At first add each 2 ml of cationic surface active agent standard solution, stopper at its each time and after shaking vigorously, stand still. When the separation of two layers becomes quick, reduce sequentially the titration amount, at near the end point carry out at each drop, and take the time when the blue of both layers has become the same with taking the white plate as the background as the end point.
- (c) Calculation Calculate the bond sulfuric acid of total anionic surface active agent according to the following formula.

$$C = \frac{D \times \frac{1}{250} \times f_c \times 80.06}{S \times 1000 \times \frac{10}{1000}} \times 100 = \frac{3.20 \times D \times f_c}{S}$$

where, C : bond sulfuric acid of total anionic surface active agent (as SO_3) (%)

D : amount of cationic surface active agent standard solution used for titration of sample solution (ml)

f_c : factor of cationic surface active agent standard solution

S : mass of sample (g)

80.06 : chemical formula weight of SO_3 .

(4.2) Determination of Bond Sulfuric Acid of Alkyl Sulfate, Alkylethoxy Sulfate, etc.

- (a) Weigh out the suitable amount of sample (including approximately 1.4 g as pure content) to the nearest 0.1 mg, add water 200 ml, dissolve by heating,

after cooling, transfer to one mark volumetric flask 250 ml and add water up to the marked line.

- (b) From this take 50 ml into an Erlenmeyer flask of 300 ml, add 0.5 mol/l (1 N) sulfuric acid 50 ml by using a transfer pipet, attach a glass tube of 65 cm or more in length and heat by hot plate or on sand bath for 3 h to dissolve.
- (c) After cooling, wash the inner wall by pouring a small amount of water from upper part of glass tube, thereafter with using phenolphthalein solution (1 w/v %) as the indicator, add 2 mol/l (2 N) sodium hydroxide solution to neutralize, thereafter add water to make 200 ml, take this as the sample solution and operate according to (4.1).
- (d) Calculation Obtain the bond sulfuric acid of alkyl sulfate, alkylethoxy sulfate, etc. according to the following formula.

$$C_A = C - C_u$$

where, C_A : bond sulfuric acid of alkyl sulfate (as SO_3) (%)
 C : bond sulfuric acid of total anionic surface active agent (as SO_3) (%)
 C_u : bond sulfuric acid of non-decomposed anionic surface active agent (as SO_3) (%).

In the case where the chemical formula weight of anionic surface active agent in sample is already known⁽⁷⁾, calculate the pure content according to the following formula.

$$P = C \times \frac{M}{80.06}$$

where, P : pure content (%)
 C : bond sulfuric acid (as SO_3) (%)
 M : chemical formula weight of anionic surface active agent
 80.06 : chemical formula weight of SO_3 .

Note ⁽⁷⁾ The chemical formula weight of anionic surface active agent to be compounded in household synthetic detergent on the market is shown in Table 2.

Table 2. Chemical Formula Weight of Anionic Surface Active Agent

Anionic surface active agent	Range of chemical formula weight	Representative value
Sodium alkylbenzenesulfonate	330 to 370	348 (number of carbons 12)
Sodium alkylsulfate	270 to 380	288 (number of carbons 12)
Sodium alkylethoxy sulfate	400 to 520	420 (number of carbons 12, EO 3 mol)
Sodium alkenyl sulfonate	300 to 370	325 (number of carbons 16)
Sodium alkylsulfonate	300 to 380	328 (number of carbons 16)

5.3.3 Determination of Soap Content

- (1) Summary As to the soap content, the water layer part obtained in 5.1.3 is acid-decomposed, the generated fatty acid is extracted by petroleum ether so as the amount to be obtained, and then the neutral value of the fatty acid is measured to be obtained.
- (2) Reagents Reagents shall be as follows.
 - (a) 0.25 mol/l (N/2) Sulfuric Acid The 0.25 mol/l (N/2) sulfuric acid specified in 4.4 (28.2) of JIS K 8001.
 - (b) Methyl Orange Solution The Methyl Orange solution specified in 4.3 of JIS K 8001.
 - (c) Petroleum Ether The petroleum ether in accordance with 5.1.2 (1).
 - (d) Sodium Sulfate (Anhydride) The sodium sulfate (anhydride) specified in JIS K 8987.
 - (e) 0.5 mol/l (N/2) Potassium Hydroxide Solution The 0.5 mol/l (N/2) potassium hydroxide solution prepared by using potassium hydroxide specified in JIS K 8574. Carry out the standardization according to 4.4 (19) of JIS K 8001. In this case, use potassium hydroxide 35 g and amide sulfate specified in JIS K 8005 of 1.20 to 1.45 g.
 - (f) Neutral Ethanol Neutralize the ethanol (95) specified in JIS K 8102, by using the phenolphthalein solution (1 w/v %) as the indicator, by 0.5 mol/l (N/2) potassium hydroxide solution. Prepare this solution just before using.
 - (g) Phenolphthalein Solution (1 w/v %) The phenolphthalein solution is in accordance with 5.1.2 (5).
- (3) Operation The operation shall be carried out as follows:
 - (a) Collect the petroleum ether extraction residual solution of 5.1.3 and washings, and, using Methyl Orange solution as indicator, add 0.25 mol/l (N/2) sulfuric acid until it becomes acidic.
 - (b) Transfer to a separatory funnel, add petroleum ether 100 ml, shake, thereafter stand still to separate into two layers, transfer the lower layer to other separatory funnel, and further extract this by petroleum ether of each 25 ml three times.
 - (c) Joint the petroleum ether layers, use Methyl Orange solution as indicator, wash with each 100 ml water until it becomes neutral, after dehydrating with sodium sulfate (anhydride), filter into an Erlenmeyer flask 300 ml of already known mass by using dried filter paper, and wash with petroleum ether.
 - (d) After removing by distilling the most part of petroleum ether on water bath, after expelling the remaining petroleum ether by feeding dry air into its inside, leave the Erlenmeyer flask to cool in a desiccator and measure the mass.
 - (e) Calculation Calculate the amount of fatty acid according to the following formula.

$$F = \frac{A}{S} \times 100$$

where, F : amount of fatty acid (%)
 A : petroleum ether extraction amount (g)
 S : mass of sample of 5.1.3 (g).

- (f) Add neutral ethanol 50 ml to Erlenmeyer flask, heat to dissolve, add phenolphthalein solution (1 w/v %) 0.5 ml as indicator, and titrate by 0.5 mol/l (N/2) potassium hydroxide solution.

Take the time when maintaining extremely faint pink color for 30 s as the end point.

- (g) Calculation Calculate the neutralization value of fatty acid according to the following formula.

$$N.V. = \frac{28.05 \times B \times f}{A}$$

where, $N.V.$: neutralization value of fatty acid

B : amount of 0.5 mol/l (N/2) potassium hydroxide solution used for titration (ml)

f : factor of 0.5 mol/l (N/2) potassium hydroxide solution

A : petroleum ether extraction amount (g)

28.05 : (chemical formula weight of potassium hydroxide) $\times \frac{1}{2}$.

Calculate the soap content as the sodium salt according to the following formula.

$$C = F \left[1 + \frac{N.V.}{2552} \right]$$

where, C : soap content (%)

F : amount of fatty acid (%)

$N.V.$: neutralization value of fatty acid

2552 : $\frac{56106}{22.990 - 1.008}$

56106 : chemical formula weight of potassium hydroxide
 56.106×1000

22.990 - 1.008 : (atomic weight of sodium) - (atomic weight of hydrogen).

Remark: Herein the soap content in sample is calculated as fatty acid sodium salt, but in the case where it is clear that it is potassium salt or triethanol amine salt, instead of 2552 in the above formula, in the case of potassium salt use 1473, and in the case of triethanol amine salt use 376.1.

5.4 Quality Test and Determination of Cationic Surface Active Agent

5.4.1 Summary As to cationic surface active agents, generally there are fatty group amine salt, fourth grade ammonium salt, alkylpyridinium salt, etc. To these, the chemical reaction same as that of 5.3.1 is utilized for quality test and determination.

5.4.2 Quality Test of Cationic Surface Active Agent

- (1) Reagents Reagents shall be as follows.

(a) Methylene Blue Solution The Methylene Blue solution is in accordance with 5.3.1 (2) (a).

(b) Chloroform The chloroform is in accordance with 5.3.1 (2) (b).

- (c) Anionic Surface Active Agent Standard Solution The anionic surface active agent standard solution is in accordance with 5.3.2 (2) (a).
- (2) Operation The operation shall be carried out as follows:
- (a) Similarly to 5.3.1 (3) enter the Methylene Blue solution and chloroform in a test tube, enter one or two drops of anionic surface active agent standard solution, and shake to make the chloroform layer clear blue.
- (b) Add to this several drops of approximately 1 w/v % (or 1 v/v %) solution of sample, shake up and down vigorously and observe the condition of chloroform layer. When the blue of chloroform layer becomes faint and as the amount of sample solution increases it becomes colorless, the fact indicates the existence of cationic surface active agent.

Remark: Method for Detecting Only Fourth Grade Ammonium Series Cationic Surface Active Agent Take bromphenol blue 0.1 mol/l (N/10), sodium hydroxide solution 5 ml, chloroform of approximately 5 ml into a test tube, add to this 1 w/v % (or 1 v/v %) solution of sample, shake vigorously, and when the separated chloroform layer becomes blue, it indicates the existence of cationic surface active agent of fourth grade ammonium series.

5.4.3 Determination of Cationic Surface Active Agent

- (1) Reagents Reagents shall be as follows:
- (a) Anionic Surface Active Agent Standard Solution The standard solution is in accordance with 5.3.2 (2) (a).
- (b) Methylene Blue Solution The Methylene Blue solution is in accordance with 5.3.1 (2) (a).
- (c) Chloroform The chloroform is in accordance with 5.3.1 (2) (b).
- (2) Apparatus Cylinder for titration The cylinder for titration shall be in accordance with 5.3.3 (3).
- (3) Operation The operation shall be carried out as follows:
- (a) Weigh out a suitable amount of sample (containing approximately 2 g as pure content) to the nearest 0.1 mg, dissolve in water to make 1 l in one mark volumetric flask and take it as sample solution.
- (b) From this take 10 ml into a cylinder for titration by using a transfer pipet, and add Methylene Blue solution 25 ml and chloroform 15 ml.
- (c) At first add each 2 ml of anionic surface active agent standard solution, at each time stopper and after shaking vigorously, stand still. When the separation of two layers becomes quick, reduce sequentially the titration amount, carry out at each one drop at near the end point, and take the time when the blue of both layers becomes the same, with taking a white plate as the background, as the end point. At the same time, carry out the blank test.
- (4) Calculation Calculate the cationic surface active agent according to the following formula.

$$C = \frac{(A - B) \times \frac{1}{250} \times f \times M \times 10}{S}$$

where, C : cationic surface active agent (%)
 A : amount of anionic surface active agent standard solution used for titration (ml)

B : amount of anionic surface active agent standard solution used for blank test (ml)

f : factor of anionic surface active agent standard solution

M : chemical formula weight of cationic surface active agent

S : mass of sample (g).

5.5 Quality Test and Determination of Nonionic Surface Active Agent

5.5.1 Summary When the aqueous solution of ethanol soluble content of 5.2 does not indicate the reaction of anionic property according to 5.3.2 nor the reaction of cationic property according to 5.4.2, it is considered that it is exclusively nonionic surface active agent. When it is possible that the anionic surface active agent or cationic surface active agent coexists, the separation by ion exchange resin or active alumina shall be carried out according to the separation systematic figures of Fig. 2 and Fig. 3.

Fig. 2. Separation Systematic Figure A
Ion Exchange Chromatography

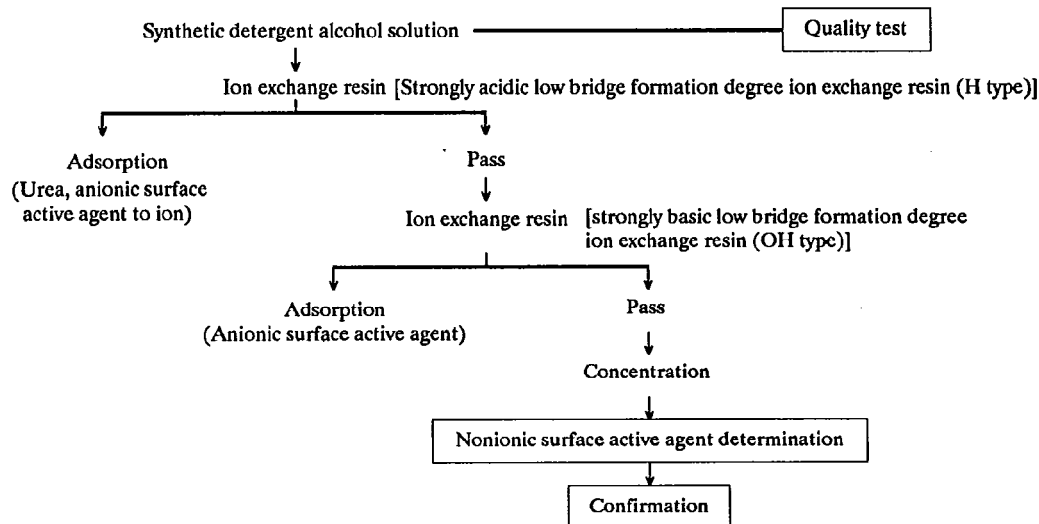
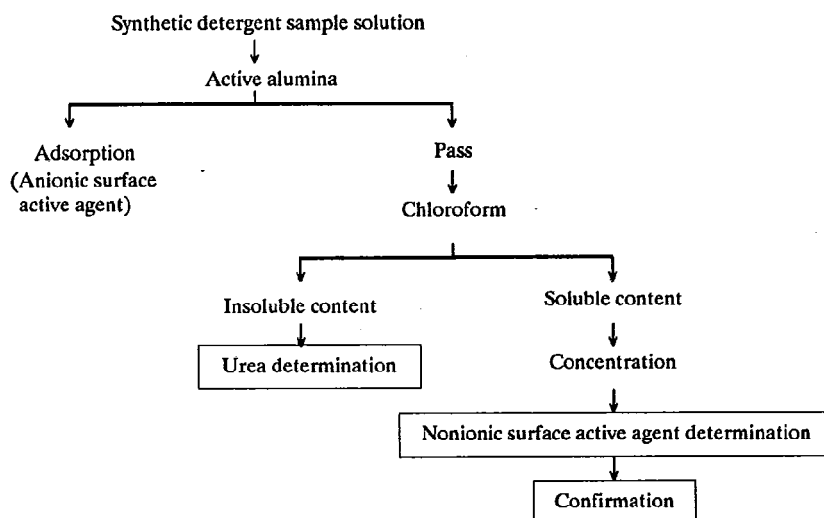


Fig. 3. Separation Systematic Figure B
Alumina Column Chromatography



5.5.2 Quality Test of Nonionic Surface Active Agent

- (1) Summary The object of this method is only the nonionic surface active agent of polyoxyethylene series. This method does not inhibit the coexistence of anionic surface active agent, but does not apply to the case of coexistence of cationic surface active agent.
- (2) Reagents Reagents shall be as follows.
 - (a) Sodium Phosphomolybdate Solution (10 w/v %) Dissolve sodium phosphomolybdate 10 g on the market in water to make 100 ml.
 - (b) Barium Chloride Solution (10 w/v %) The barium chloride solution specified in 4.1 of JIS K 8001.
 - (c) Hydrochloric Acid (1 + 10) Prepare by using hydrochloric acid specified in JIS K 8180.
- (3) Operation The operation shall be carried out as follows:
 - (a) Take 1 w/v % (or 1 v/v %) solution 5 ml of sample into a test tube, add hydrochloric acid (1 + 10) 10 ml and barium chloride solution (10 w/v %) 10 ml and heat.
 - (b) When turbidity or precipitate is generated, filter this, and add sodium phosphomolybdate solution (10 w/v %) 1 ml to the filtrate.
 - (c) When nonionic surface active agent coexists slight yellow precipitate is generated.

5.5.3 Determination of Nonionic Surface Active Agent5.5.3.1 Ion Exchange Chromatography

- (1) Summary By using anionic exchange resin and cationic exchange resin, the anionic surface active agent and cationic surface active agent are separated and the nonionic surface active agent and the nonionic surface active agent to be eluted is determined.
- (2) Reagents Reagents shall be as follows.
 - (a) Ethanol (95) The ethanol specified in JIS K 8102.
 - (b) Strongly Acidic Cation Exchange Resin The strongly acidic low bridge formation degree ion exchange resin (H type).
 - (c) Strongly Basic Anion Exchange Resin The strongly basic low bridge formation degree ion exchange resin (OH type).

Informative Reference: As to the ion exchange resin, the following matters are on the market.

- (1) Strongly Acidic Cation Exchange Resin There are Dowex 50 WX 2, Dowex 50 WX 4, Amberlite XE-100, Dia ion SK 102, SK 104, etc. The grain size is 297 to 149 μm .
- (2) Strongly Basic Anion Exchange Resin There are Dowex 1 X 2, Dowex 1 X 4, Amberlite IRA-401, Dia ion SA 101, etc. The grain size is 297 to 149 μm .
- (3) Apparatus Apparatuses shall be as follows:
 - (a) Tube for Column The bore is 1 cm and the length is approximately 30 cm. The bottom part is filled with glass wool.
 - (b) Beaker 500 ml
 - (c) Separatory Funnel 100 ml
 - (d) Oven The oven in accordance with 5.2.3 (4).

- (4) Preparation of Column Flow the ion exchange resin to be used with ethanol (95) respectively into tube for column to fill, and make the height 15 to 20 cm. Assemble the column filled with strongly acidic cation exchange resin on the upper, and the column filled with strongly basic anion exchange resin on the lower.
- (5) Operation The operation shall be carried out according to Fig. 2 Separation Systematic Figure A of 5.5.1.
- (a) Transfer the ethanol solution 100 ml obtained in 5.2.4 (2) to a separatory funnel from the beaker, flow gradually from the separatory funnel to column and receive the eluate in a beaker 500 ml.
- (b) Flow ethanol (95) 200 to 250 ml to wash the inside of column, join the washings with the eluate, heat on water bath to remove the ethanol, put into an oven adjusted at $105 \pm 2^\circ\text{C}$ to dry until becoming constant amount, and weigh the mass.
- (6) Calculation Calculate the nonionic surface active agent according to the following formula.

$$C = \frac{A \times \frac{250}{100}}{S} \times 100 - D = \frac{A \times 250}{S} - D$$

where, C : nonionic surface active agent (%)
 A : amount of eluate (g)
 S : mass of sample of 5.2.4 (g)
 D : petroleum ether soluble content (%).

5.5.3.2 Alumina Column Chromatography

- (1) Summary The synthetic detergent is separated to adsorption substance and non-adsorption substance according to alumina column chromatography, and the chloroform soluble content in nonadsorption substance is taken as the amount of nonionic surface active agent.
- (2) Reagents Reagents shall be as follows:
- (a) Mixed Solvent Mix the ethyl acetate specified in JIS K 8361 and the methanol specified in JIS K 8891 in volume ratio of 1 : 1.
- (b) Active Alumina The active alumina for chromatograph (43 to 74 μm).
- (3) Apparatus The apparatus shall be as follows.
- (a) Tube for Column A tube of 2.5 cm in bore and 35 cm in length, attached with a glass cock.
- (b) Separatory Funnel 300 ml
- (c) Erlenmeyer Flask 100 ml, 500 ml
- (d) Oven The oven in accordance with 4.2.3 (4).
- (4) Preparation of Column Fill⁽⁸⁾ the absorbent cotton or glass wool in the top end of tube for column, so as the filler not to flow out. Take active alumina 80 to 100 g into a beaker, suspend with mixed solvent, flow into a tube for column so as air bubbles not to enter, and fill up to the height of 60 to 70 % of tube for column. After precipitation of active alumina, press its upper part with filter paper or cotton stopper, open the cock to flow out gradually the mixed solvent, and remain a small amount of mixed solvent at the upper part to such degree that air bubbles are not generated.

Note ⁽⁸⁾ After filling absorbent cotton or glass wool, after placing sea sand of 5 mm degree, if flow-in active alumina, the filling becomes easy.

- (5) Operation The operation shall be carried out as follows according to Fig. 3 Separation Systematic Figure B of 5.5.1:
- Weigh out the sample⁽⁹⁾ 2 to 3 g⁽¹⁰⁾ to the nearest 0.1 mg, dissolve in mixed solvent⁽¹¹⁾ of as small amount as possible and transfer to column.
 - Open the cock, and flow out the mixed solvent to the degree not to generate air bubbles at the upper part. Wash the beaker with a small amount of mixed solvent and repeat this operation twice.
 - Next, connect the separatory funnel containing the mixed solvent 300 ml with the column, flow out at a speed of 0.3 to 0.5 ml/min, and receive⁽¹²⁾ in an Erlenmeyer flask 500 ml.
 - Heat on a water bath to remove the mixed solvent, transfer to the Erlenmeyer flask 100 ml of already known mass, again heat on water bath to remove the mixed solvent, thereafter enter in an oven adjusted at $105 \pm 2^\circ\text{C}$ to dry until becoming constant amount and weigh the mass.
 - Calculation Calculate the alumina column eluate content according to the following formula.

$$C_E = \frac{A_E}{S} \times 100$$

where, C_E : alumina column eluate content (%)
 A_E : alumina column eluate amount (g)
 S : mass of sample (g).

- Next, add chloroform approximately 40 ml to the column eluate to heat, and in the case where insoluble matter is generated, obtain the mass of chloroform soluble matter according to 5.6.1.
- Calculation Calculate the nonionic surface active agent according to the following formula.

In the Case Where No Chloroform Insoluble Matter Is Generated

$$C = C_E - D$$

where, C : nonionic surface active agent (%)
 C_E : alumina column eluate content (%)
 D : petroleum ether soluble content (%).

In the Case Where Chloroform Insoluble Matter Is Generated

$$C = \frac{A}{S} \times 100 - D$$

where, C : nonionic surface active agent (%)
 A : chloroform soluble amount (g)
 S : mass of sample (g)
 D : petroleum ether soluble content (%).

- Notes (9) In the case where the sample is pulver state or grain state, collapse them in a mortar, and in the case where the sample is liquid, remove the moisture as far as possible according to azeotropy or the like with ethanol on water bath.
- (10) In the case where anionic surface active agent coexists, take the sample so that it becomes not more than 700 mg as anionic surface active agent.
- (11) In the case where nonsoluble matter to mixed solvent exists, after suspending transfer to column.
- (12) After transferring the sample to column, collect the eluate over the whole operation.

5.5.4 Confirmation of Nonionic Surface Active Agent

- (1) Summary The eluate obtained by ion exchange chromatography or alumina column chromatography is separated according to thin layer chromatography, and the existence of nonionic surface active agent of polyoxyethylene series and nonionic surface active agent of alkylolamide series is confirmed.
- (2) Reagents Reagents shall be as follows.
 - (2.1) Silica Gel for Thin Layer Chromatography The silica gel containing calcium sulfate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) approximately 13 %.
 - (2.2) Coloring Reagents (Dragendorff varied method reagent)
 - (a) Acetic Acid (30 v/v %) The acetic acid prepared by using acetic acid specified in JIS K 8355.
 - (b) The matter made by dissolving basic bismuth nitrate 0.85 g specified in JIS K 8169 in acetic acid (30 v/v %) 100 ml and adding water 40 ml.
 - (c) The matter made by dissolving potassium iodide 8 g specified in JIS K 8913 in water 20 ml.
 - (d) Above-mentioned (a), (b), (c) and water are mixed at volumetric ratio of 1 : 1 : 4 : 10 directly before using.
 - (2.3) Development Solvent Enter the solvent mixed with ethyl acetate specified in JIS K 8361, acetone specified in JIS K 8034 and water at volumetric ratio of 55 : 35 : 10 in a development tank, and saturate the inside of tank with solvent vapor.
- (3) Thin Layer Plate Prepare a thin layer plate of 0.3 mm in thickness, after drying in air to hardness, carry out activation in an oven at 120°C for 1.5 h, and preserve in a tightly sealed container containing desiccating agent.
- (4) Operation The operation shall be carried out as follows:
 - (a) Make the eluate obtained in 5.5.3.1 (5) or 5.5.3.2 (5) approximately 5 w/v % solution with ethanol (95), and spot this solution approximately 5 μl by using micropipet at the position of approximately 1.5 to 2 cm from the lower end of thin layer plate.
 - (b) After air drying, enter in a development tank, and develop up to the height of approximately 17 cm from the origin. The development temperature should preferably be about 25°C.
 - (c) After air drying or drying in a drier the plate after developing, spray uniformly the coloring reagent. When having detected many spots colored to orange or reddish orange on the yellow substrate, the existence of nonionic surface active agent of polyoxyethylene series is anticipated⁽¹³⁾.