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SECTION III. GLYCERINES

SECTION IV. ALKALINE SOAPS

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3.121 DETERMINATION OF THE GLYCEROL CONTENT
(TITRIMETRIC METHOD)
(Fifth Edition : Method III.A.1)

1. SCOPE

This Standard describes a titrimetric method for the determination of the glycerol content of industrial glycerines.

2. FIELD OF APPLICATION

This Standard is not applicable in the presence of organic compounds containing more than two hydroxyl groups on adjacent carbon atoms such as sugars as these compounds may also give rise to formic acid and, for this reason, will interfere in the determination.

3. DEFINITION

The glycerol content is the quantity of glycerol expressed as a percentage (m/m), and determined by the present method.

4. PRINCIPLE

Cold oxidation of the glycerol by sodium periodate in a strongly acid medium. Titration of the formic acid (produced by the reaction) with a standard solution of sodium hydroxide, using a pH meter.

5. REACTION

$$CH_2OH-CHOH-CH_2OH + 2\ NaIO_4 \longrightarrow HCOOH + 2\ HCOH + 2\ NaIO_3 + H_2O$$

6. APPARATUS

Cork stoppers should not be used and ground-glass joints are recommended.

6.1.   500 ml conical flasks

6.2.   600 ml tall-form beakers

6.3.   50 ml burette with the jet drawn out so as to allow delivery of 30 drops per ml

6.4.   500 ml volumetric flask

6.5.   1000 ml volumetric flask

6.6.   50 ml graduated pipette

6.7.   pH meter, fitted with a glass electrode.   (Note 1)

6.8.   Stirrer, preference should be given to a magnetic stirrer.   In this case check that it does not influence the pH meter

7. REAGENTS

7.1.   Distilled water, or water of equivalent purity, free from carbon dioxide

7.2.   Ethylene glycol (1,2-ethanediol) free from glycerol, solution in distilled water (7.1) 1 : 1 (V/V)

7.3.   Sulphuric acid, aqueous solution, approximately 0.1 N

7.4.   Sodium hydroxide, aqueous solution, approximately 0.05 N

7.5.   Sodium metaperiodate, neutral, titre at least 98 per cent (m/m), aqueous acid solution 60 g/l.   (Note 2)

7.6.   Sodium formate, aqueous solution, approximately 1 N

7.7. Sodium hydroxide, 0.1 N aqueous solution, accurately standardised

7.8. Sodium hydroxide, 0.125 N aqueous solution, accurately standardised, free from carbon dioxide. (Note 3)

7.9. Potassium hydrogenphthalate $C_6H_4(COOK)(COOH)$, 0.05 M aqueous solution (10.12 g/l, pH 4.00 at 20°C). (Note 4)

7.10. Disodium tetraborate decahydrate ($Na_2B_4O_7$, 10 H_2O), 0.01 M aqueous solution (3.81 g/l, pH 9.22 at 20°C). (Note 4)

7.11. Phenolphthalein, 5 g/l solution in 95 per cent (V/V) ethanol

7.12. Phenol red

8. PROCEDURE

As the presence of carbon dioxide can introduce errors, it is advisable to cover the vessels containing the test solutions with a clock glass during the standing periods and also to avoid enriching the carbon dioxide content of the laboratory atmosphere by other operations carried out at the same time.

8.1. TEST PORTION

In the case of alkaline samples or samples giving a tarry precipitate on acidification, the procedure indicated under the particular case is to be used.

8.1.1. General case

If the approximate glycerol content is not known, it should be determined by a preliminary test on 0.50 g of the sample.

Case of glycerines whose glycerol content is not higher than 75 per cent

Weigh, to the nearest 0.0001 g, a test portion containing 0.30 to 0.50 g of glycerol. Transfer quantitatively to a beaker (6.2) for determination.

Case of glycerines whose glycerol content is higher than 75 per cent

Weigh, to the nearest 0.0001 g, 5 g ± 0.1 g of the test sample. Transfer quantitatively to a volumetric flask (6.4). Dilute to 500 ml with distilled water (7.1) and mix. Transfer by pipette 50 ml of this solution to a beaker (6.2) for determination.

8.1.2. Particular case

Transfer the test portion prepared as indicated in the general case to an appropriate vessel. Dilute to 50 ml if necessary. In the presence of 2 drops of the phenolphthalein solution (7.11), neutralise just to decoloration by means of the sulphuric acid solution (7.3). Add a 5 ml excess of the sulphuric acid solution (7.3). Fit a reflux condenser. Bring to the boil and maintain boiling for 5 minutes.
Allow to cool. If necessary, filter and wash with water (7.1). Transfer quantitatively the solution obtained to a beaker (6.2) for determination.

8.2. BLANK TEST

Carry out, at the same time as the determination and under the same conditions, a blank test without the test portion using the same quantities of reagents and diluting water as for the determination.

8.3. DETERMINATION

Dilute the test sample in the beaker (6.2) with water (7.1) to a volume of about 250 ml. Insert the glass electrode and start stirring with the stirrer (6.8). Neutralise by means of the sodium hydroxide solution (7.4) to pH 7.9 ± 0.1 checked by the pH meter (6.7). With a pipette (6.6) add 50 ml of the sodium metaperiodate solution (7.5). Mix with moderate agitation. Cover the beaker with a clock glass and allow to stand for 30 minutes in the dark at a temperature not exceeding 35°C.
Add 10 ml of the ethylene glycol solution (7.2). Mix. Allow to stand for 20 minutes in the dark at a temperature not exceeding 35°C.
Add 5.00 ml of the sodium formate solution (7.6) with a graduated pipette (6.6). With the burette (6.3), titrate the acidity present with the sodium hydroxide solution (7.8) to a pH 7.9 ± 0.2, checked with the pH meter (6.7).

9. EXPRESSION OF RESULTS

The glycerol content, expressed as a percentage (m/m), is given by the formula :

$$(V_1 - V_2) \times T \times 0.0921 \times \frac{100}{m}$$

where

V_1 is the number of ml of the sodium hydroxide solution (7.8) used for the determination,

V_2 is the number of ml of the sodium hydroxide solution (7.8) used for the blank test,

T is the exact normality of the sodium hydroxide solution (7.8) used,

m is the mass, in g, of glycerine subjected to the reaction with the sodium metaperiodate solution (7.5).

10. NOTES

1. The pH meter should be checked by means of two buffer solutions (7.9) and (7.10).

2. Sodium metaperiodate

2.1. Verification of the sodium metaperiodate neutrality :

In a conical flask (6.1), dissolve 5 g of sodium metaperiodate in 150 ml of water (7.1). Add 5 ml of ethylene glycol (7.2). Allow to stand in the dark and protected from atmospheric carbon dioxide for 30 minutes.
Under these conditions, it should be possible to neutralise the solution in the presence of phenol red (7.12) with a sodium hydroxide (7.7) volume less than 1 ml and preferably less than 0.2 ml.

2.2. Preparation of the acidic solution :

Weigh, to the nearest 0.1 g, 60 g of sodium metaperiodate (7.5). Dissolve, in the cold, with 120 ml of a solution of sulphuric acid (7.3) diluted in 500 ml of water (7.1). Transfer to a volumetric flask (6.5), dilute to 1000 ml with water (7.1) and mix. If necessary filter through a sintered glass filter.

2.3. Verification of the solution acidity :

The volume of the sodium hydroxide solution (7.8) used during the blank test (8.2) should not be less than 4.5 ml, thus corresponding to the acidity required for reaction (5).

2.4. Storage of the solution :

Store the solution in a dark glass flask fitted with a ground glass stopper.

3. Until a primary standard acid be established internationally, it is recommended to interested parties that the standardisation of the solution (7.8) be carried out by means of the same batch of primary standard.

4. Use standard materials specially prepared for pH measurements.

IV. ALKALINE SOAPS   1982

4.201   DETERMINATION OF THE TOTAL ALKALI CONTENT

(Fifth Edition : Method IV.A.5)

1. SCOPE

This Standard describes two methods for the determination of the total alkali content of soaps, excluding compounded products. (Note 1).

2. DEFINITION

The total alkali content is the quantity of alkaline elements combined as soaps with fatty and resin acids, as well as those corresponding to free caustic alkali or carbonates and eventually to added products (silicates, phosphates), and determined under the conditions of the present methods.
It is expressed as a percentage (m/m) of sodium hydroxide or potassium hydroxide according to whether sodium or potassium soaps are concerned.

3. TITRIMETRIC METHOD   (Note 1)

3.1. Field of application

This method is not applicable to soaps artificially coloured by water soluble colouring matters, or to soaps containing calcium carbonate or, more generaly, acid decomposed substances.

3.2. Principle

Reaction of the alkaline compounds with a known amount of strong acid, added in excess, liberating fatty acids. Removal of the fatty acids by extraction with diethyl ether and determination of the excess of strong acid by titration with aqueous sodium hydroxide.

3.3. Apparatus

3.3.1.   500 ml conical flask

3.3.2.   250 ml beaker

3.3.3.   500 ml separating funnels

3.4. Reagents

3.4.1.   Diethyl ether

3.4.2.   Sodium chloride, 100 g/l aqueous solution

3.4.3.   Sulphuric acid, 1 N aqueous solution, accurately standardised

3.4.4.   Sodium hydroxide, 1 N aqueous solution, accurately standardised

3.4.5.   Methyl orange, 1 g/l aqueous solution

3.5. Procedure

Into a beaker (3.3.1), weigh to the nearest 0.01 g, about 5 to 10 g of soap. Add 100 ml of distilled water. Gently heat until complete dissolution.
Transfer quantitatively to a separating funnel (3.3.2). Add a few drops of methyl orange (3.4.4). Add an exactly known volume of sulphuric acid (3.4.2) until the methyl orange (3.4.4) becomes red. Allow to cool at room temperature.
Add 100 ml of diethyl ether (3.4.1). Shake vigorously for 1 minute. Allow to stand until the two phases are completely separated.
Draw off quantitatively the aqueous acid solution into a second separating funnel (3.3.3).
Carry out a second extraction of the acid solution similarly, shaking with 50 ml of diethyl

ether (3.4.1). Draw off quantitatively the aqueous acid solution into a conical flask (3.3.1) (Note 1). Combine the two ethereal solutions in the first separating funnel. Wash twice with 50 ml of the sodium chloride solution (3.4.2) shaking for 1 minute in each case. Add quantitatively the washings to the aqueous acid solutions in the conical flask. Titrate the acidity of the contents of the conical flask with sodium hydroxide solution (3.4.4).

3.6. Expression of results

The total alkali content, expressed as a percentage (m/m), is given by the formula :

$$\frac{4.0 \times \left[(V_1 \times T_1) - (V_2 \times T_2)\right]}{m} \text{ , for a sodium soap,}$$

or by the formula :

$$\frac{5.6 \times \left[(V_1 \times T_1) - (V_2 \times T_2)\right]}{m} \text{ , for a potassium soap,}$$

where :

V_1 is the number of ml of the sulphuric acid solution (3.4.2) used

V_2 is the number of ml of the sodium hydroxide solution (3.4.3) used

T_1 is the exact normality of the sulphuric acid solution (3.4.2) used

T_2 is the exact normality of the sodium hydroxide solution (3.4.3) used

m is the mass, in g, of the test portion

4. INCINERATION METHOD

4.1. Field of application

Method of general application. To be used when an investigation of the ash is necessary.

4.2. Principle

Incineration of the test portion. Determination of the alkaline elements contained in the ash.

4.3. Apparatus

4.3.1. 250 ml conical flask

4.3.2. Porcelain or glass incineration dish with diameter about 11 cm

4.3.3. 100 ml volumetric flask

4.3.4. Graduated pipette 50 ml

4.4. Reagents

4.4.1. Sulphuric acid, 0.5 N, aqueous solution accurately standardised

4.4.2. Methyl orange, 1 g/l aqueous solution

4.5. Procedure

Weigh, to the nearest 0.01 g, about 10 g of soap into an incineration dish (4.3.2). Incinerate cautiously until a black ash is obtained.
By means of warm distilled water, transfer quantitatively to a volumetric flask (4.3.3). Allow to cool.
Make up to 100 ml with distilled water. Shake to mix. Filter through a dry filter. By means of a pipette (4.3.4), transfer 50 ml of the filtrate to a conical flask (4.3.1). Titrate with sulphuric acid (4.4.1) in the presence of methyl orange (4.4.2).

4.6. Expression of results

The total alkali content, expressed as a percentage (m/m), is given by the formula :

$$\frac{8.0 \times V \times T}{m} \text{ , for a sodium soap}$$

or by the formula :

$$\frac{11.2 \times V \times T}{m} \text{ , for a potassium soap}$$

where :

        V is the number of ml of the sulphuric acid solution (4.4.1) used

        T is the exact normality of the sulphuric acid solution (4.4.1) used

        m is the mass, in g, of the test portion

5. NOTE

1. If the simultaneous determination of the total alkali content and of the total crude fatty acids content is required, the ether solutions which appear in the titrimetric method given hereunder may be used.
In this case, they should be combined and the analysis should be carried out as indicated in the procedure of method 4.211 from " Combine the ether solutions in the same separating funnel ... ".
This possibility is offered only in the limits of the titrimetric method field of application.

IV. ALKALINE SOAPS   1982

4.202 DETERMINATION OF THE FREE CAUSTIC ALKALI CONTENT

(Fifth Edition : Method IV.A.7)

1. SCOPE AND FOREWORD

This Standard describes two methods for the determination of the free caustic alkali content in commercial soaps, excluding compounded products.
As soaps usually contain a small amount of unsaponified neutral fat, there is no perfect procedure for determining free caustic alkali because, when the sample of soap is dissolved, the neutral fat is more or less saponified by any free caustic alkali present.
Both methods described are therefore of an empirical nature.

2. ETHANOL METHOD

2.1. Field of application

The ethanol method should be applied only to sodium soaps of ordinary quality, as the presence of certain additions brings in sources of error. It is not applicable to potassium soaps because of the solubility of potassium carbonate in ethanol.

2.2. Definition

The free caustic alkali content of sodium soaps of ordinary quality is the quantity of free caustic alkali, expressed as a percentage (m/m) of sodium hydroxide, and determined by the present method.

2.3. Principle

Dissolution of the soap in absolute ethanol, free from carbon dioxide and neutralised.
Determination of the alkalinity with a standardised solution of hydrochloric acid.

2.4. Apparatus

2.4.1. 250 ml conical flask

2.4.2. Reflux condenser to fit the flask (2.4.1)

2.5. Reagents

2.5.1. Ethanol, absolute

2.5.2. Potassium hydroxide, ethanolic solution, approximately 0.1 N

2.5.3. Hydrochloric acid, 0.1 N ethanolic solution, accurately standardised

2.5.4. Phenolphthalein, 10 g/l solution in 95 per cent (V/V) ethanol

2.6. Procedure

Pour 200 ml of ethanol (2.5.1) into the flask (2.4.1). Connect the reflux condenser (2.4.2).
Bring to a gentle boil and keep at the boil for 5 minutes in order to remove carbon dioxide.
Remove the reflux condenser (2.4.2) and allow to cool to about 70°C.
Add 4 drops of phenolphthalein solution (2.5.4). Neutralise with the potassium hydroxide solution (2.5.2) until the indicator just turns pink. Weigh, to the nearest 0.01 g, about 5 g of soap. Transfer quantitatively the test portion to the flask (2.4.1) containing the neutralised ethanol. Connect the reflux condenser (2.4.2). Allow to boil gently until the soap is completely dissolved.
Allow to cool to about 70°C.
Titrate with the hydrochloric ethanolic solution (2.5.3) until the indicator just turns pink as in the case of the ethanol neutralisation.

2.7. Expression of results

The free caustic alkali content, expressed as a percentage (m/m) of sodium hydroxide, is given by the formula :

$$\frac{4.0 \times V \times T}{m}$$

where :

V is the number of ml of the standardised hydrochloric acid solution (2.5.3) used

T is the exact normality of the hydrochloric acid solution (2.5.3) used

m is the mass, in g, of the test portion

3. BARIUM CHLORIDE METHOD

3.1. Field of application

The barium chloride method should be applied to all soft potassium soaps or to mixed potassium and sodium soaps.

3.2. Definition

The free caustic alkali content of soft soaps is the quantity of free caustic alkali, expressed as a percentage (m/m) of potassium hydroxide, and determined by the present method.

3.3. Principle

Precipitation of carbonates and fatty acids by barium chloride. Determination of the residual alkalinity with a hydrochloric acid solution exactly standardised. (Note 1).

3.4. Apparatus

3.4.1. 500 ml conical flask

3.4.2. Reflux condenser to fit the flask (3.4.1)

3.5. Reagents

3.5.1. Distilled water or water of at least equivalent purity, free from carbon dioxide

3.5.2. Ethanol, 95 per cent (V/V), free from carbon dioxide and distilled over potassium hydroxide

3.5.3. Ethanol, aqueous solution 60 per cent (V/V), neutralised
Mix 125 ml ethanol (3.5.2), 75 ml distilled water (3.5.1) and 1 ml of indicator (3.5.7). Neutralise to a violet colour with an aqueous solution of potassium or sodium hydroxide (3.5.4). Heat under reflux for 10 minutes. Allow to cool to room temperature. Add 1 ml of indicator (3.5.7). Neutralise with the hydrochloric acid solution (3.5.6) until the violet colour disappears.

3.5.4. Potassium or sodium hydroxide, 0.1 N aqueous solution

3.5.5. Barium chloride, aqueous solution
Dissolve 10 g of barium chloride dihydrate ($BaCl_2$, $2H_2O$) in 90 ml of distilled water (3.5.1). Neutralise with potassium or sodium hydroxide (3.5.4) in the presence of indicator (3.5.7) until a violet colour appears.

3.5.6. Hydrochloric acid, 0.1 N aqueous solution, accurately standardised

3.5.7. Indicator mixture, phenolphthalein-thymol blue, ethanolic solution
Dissolve 1 g of phenolphthalein and 0.5 g of thymol blue in 100 ml of hot ethanol (3.5.2). Filter.

3.6. Procedure

Weigh, to the nearest 0.01 g, about 5 g of soft soap into a conical flask (3.4.1). Add 200 ml of ethanol (3.5.3). Connect the reflux condenser (3.4.2). Bring to the boil for 10 minutes. (Note 1).
Add to this boiling solution 20 ml of barium chloride solution (3.5.5) in small portions shaking thoroughly. Cool with running water to room temperature.
Add 1 ml of the indicator mixture (3.5.7). Titrate immediately with the hydrochloric acid solution (3.5.6) until the violet colour disappears.

3.7. Expression of results

The free caustic alkali content, expressed as a percentage (m/m) of potassium hydroxide, is given by the formula :

$$\frac{5.6 \times V \times T}{m}$$

where :

V is the number of ml of hydrochloric acid solution (3.5.6) used

T is the exact normality of the hydrochloric acid solution (3.5.6) used

m is the mass, in g, of the test portion

4. NOTE

1. To soft soaps containing small quantities of free fatty acids instead of free caustic alkali, add before precipitating with the barium chloride, an excess of 0.1 N ethanolic potassium hydroxide solution of exactly known normality.
   Follow the procedure as indicated.
   Calculate the free fatty acids as oleic acid.

IV. ALKALINE SOAPS   1982

4.203   DETERMINATION OF THE TOTAL FREE ALKALI CONTENT
(Fifth Edition : Method IV.A.6)

1. SCOPE

This Standard describes a method for the determination of the total free alkali content of commercial soaps excluding compounded products.

2. FIELD OF APPLICATION

This Standard is not applicable if the soap contains additives (alkali silicates, ...) which can be decomposed by fatty acids under the conditions of operation. (Note 1).

3. DEFINITION

The total free alkali content is the quantity of free caustic alkali and carbonated alkali expressed as a percentage (m/m) as either sodium hydroxide for sodium soaps or potassium hydroxide for potassium soaps.

4. PRINCIPLE

Neutralisation of the total free alkali by boiling under reflux with a known amount of fatty acids, added in excess. Determination of the excess of fatty acids by titration with ethanolic potassium hydroxide solution.

5. APPARATUS

5.1.   250 ml conical flask

5.2.   Reflux condenser to fit the flask (5.1)

6. REAGENTS

6.1.   Ethanol, 80 per cent (V/V) aqueous solution, free from carbon dioxide. (Note 2)

6.2.   Liquid fatty acids of any origin free from mineral acids

6.3.   Potassium hydroxide, 0.1 N ethanolic solution, accurately standardised

6.4.   Phenolphthalein, 10 g/l solution in 95 per cent (V/V) ethanol

7. PROCEDURE

Weigh into the flask (5.1), to the nearest 0.01 g, about 5 g of soap. Add about 5 g of fatty acids (6.2), weighed to the nearest 0.001 g. (Note 3). Add 100 ml of ethanol (6.1). Connect the reflux condenser (5.2). Warm gently until the soap is completely dissolved.
Allow to boil gently for 5 minutes.
Allow to cool to room temperature.
Titrate with the potassium hydroxide (6.3) in the presence of phenolphthalein (6.4). Simultaneously, carry out a blank test under the same conditions without soap but with the same quantity of fatty acids.
Carry out two determinations for the same sample.

8. EXPRESSION OF RESULTS

The total free alkali content is given by the formula :

$$\frac{4.0 \times T \times (V_2 - V_1)}{m} \text{ , in the case of sodium soaps,}$$

and by the formula :

$$\frac{5.6 \times T \times (V_2 - V_1)}{m} \text{ , in the case of potassium soaps,}$$

where :

V_1 is the number of ml of the potassium hydroxide solution (5.3) used for the test with the soap

V_2 is the number of ml of the potassium hydroxide solution (5.3) used for the blank test

T is the exact normality of the potassium hydroxide solution (5.3) used

m is the mass, in g, of the test portion

Consider as the result the arithmetic mean of the duplicate determinations.

9. NOTES

1. Sodium thiosulphate and calcium carbonate do not affect the results.

2. In order to eliminate the carbon dioxide :
    - bring to the boil for 5 minutes under a reflux condenser
    - allow to cool to room temperature
    - neutralise with an ethanolic potassium hydroxide solution approximately 0.1 N in the presence of phenolphthalein.

3. For some soaps having a high total free alkali content, the weight of the liquid fatty acids used should be increased.

IV. ALKALINE SOAPS   1982

4.211 DETERMINATION OF THE "TOTAL CRUDE FATTY ACIDS" CONTENT

(Fifth Edition : Method IV.A.4)

1. SCOPE

This Standard describes a method for the determination of the "total crude fatty acids" content in commercial soaps. (Note 1).

2. FIELD OF APPLICATION

This Standard is not applicable to commercial soaps containing synthetic surface agents and to compounded products.

3. DEFINITION

By definition, the "total crude fatty acids" include the water insoluble fatty matter obtained by decomposing a soap with a strong mineral acid under the conditions specified. The "total crude fatty acids" contain with the pure fatty acids, the insaponifiable together with the neutral fatty matter and the rosin acids contained in the soap. The "total crude fatty acids" content of a soap is expressed as a percentage (m/m).

4. PRINCIPLE

Decomposition of the soap by a strong acid.
Extraction of the fatty matter by diethyl ether. Evaporation of the diethyl ether. Dissolution of the residue in ethanol and neutralisation of the acids by sodium hydroxide. Weighing of the dry product obtained.

5. APPARATUS

5.1. 250 ml beakers

5.2. 500 ml separating funnels

5.3. Evaporating apparatus, for example, rotary evaporator

5.4. Boiling-water bath

5.5. Oven, regulated at 120 $\pm$ 2°C

6. REAGENTS

6.1. Ethanol 95 per cent (V/V)

6.2. Diethyl ether free from peroxides and residue

6.3. Sulphuric acid, aqueous solution 4 : 1 (V/V) or hydrochloric acid, aqueous solution (ρ = 1.13 g/ml)

6.4. Sodium chloride, 100 g/l aqueous solution

6.5. Sodium hydroxide, 0.5 N ethanolic solution, accurately standardised. (Note 2)

6.6. Methyl orange, 1 g/l aqueous solution

6.7. Phenolphthalein, 10 g/l solution in ethanol (6.1)

7. PROCEDURE

Weigh, to the nearest 0.01 g, into a beaker (5.1) about 5 g of soap. Add 100 ml of distilled water. Heat gently until complete dissolution.
Transfer quantitatively into a separating funnel (5.2). Add a few drops of the methyl orange (6.6). Add 10 ml the aqueous acid solution (6.3). The indicator should turn red. If this is not the case, add more aqueous acid solution (6.3). Allow to cool at room temperature.

Add 100 ml of diethyl ether (6.2). Shake thoroughly for 1 minute. Allow to stand until the 2 phases are completely separated.

Run off the aqueous acid layer into a second separating funnel (5.2). Carry out a second extraction of this aqueous solution with 50 ml of diethyl ether (6.2). Observe the same conditions as previously for extracting and standing. Run off the aqueous acid layer.

Combine the ether solutions in the same separating funnel (5.2). Wash with 50 ml of the sodium chloride solution (6.4), shaking for 1 minute. Repeat this washing once more. Check the neutrality of the second washing with the methyl orange (6.6). If necessary, repeat the washing until neutrality. Tare the evaporator flask of the apparatus (5.3). After the funnel washing has been run off, filter the ethereal solution through a filter paper and collect the filtrate in the tared evaporator flask. Wash the filter with small quantities of diethyl ether (6.2). Evaporate off nearly all the diethyl ether (6.2).

Neutralise 20 ml of ethanol (6.1) with the solution of sodium hydroxide (6.5) in the presence of phenolphthalein (6.7). Use this ethanol for dissolving the evaporation residue. Neutralise the fatty acids of the ethanolic solution obtained with the sodium hydroxide solution (6.5). Evaporate the ethanol on a boiling-water bath (5.4).

Place the evaporator flask in the oven (5.5) regulated at 120 $\pm$ 2°C until a constant mass is obtained (about 30 minutes).

By weighing determine the mass of the dry soaps obtained.

8. EXPRESSION OF RESULTS

The total crude fatty acids content, expressed as a percentage by mass (m/m), is given by the formula :

$$\frac{100 \times \left[m_1 - (0.022 \times T \times V)\right]}{m}$$

where :

      V is the number of ml of the sodium hydroxide solution (6.5) used

      T is the exact normality of the sodium hydroxide solution (6.5) used

      m is the mass, in g, of the test portion

      m_1 is the mass, in g, of the dry soap

9. NOTES

1. Whenever a simultaneous determination of the total crude fatty acids content and of the total alkali content is required, the procedure of the present method and of method 4.201 (titrimetric method) may be combined. See note 1 of method 4.201. This possibility can be applied only within the field of application limits of the titrimetric method for the determination of the total alkali content.

2. Do not use a potassium hydroxide solution.

IV. ALKALINE SOAPS   1982

4.212 DETERMINATION OF THE ROSIN CONTENT

(Fifth Edition : Method IV.A.9)

1. SCOPE AND FIELD OF APPLICATION

This Standard describes two methods for the determination of the rosin acids (rosin) content of commercial soaps. (Note 1).
In the case of highly coloured mixtures where the changing of the indicator is difficult to determine, the potentiometric method should be used.

2. DEFINITION

The rosin content is the quantity of rosin acids expressed as a percentage (m/m), and determined by the present methods.

3. TITRIMETRIC METHOD

3.1. Principle

Preparation of the "insoluble crude acids". Transformation to their methyl esters the nonrosin acids contained in the "insoluble crude acids". After this treatment, titration of the free acidity.

3.2. Apparatus

3.2.1.   50, 100 and 250 ml round-bottomed flasks

3.2.2.   Reflux condenser to fit flasks (3.2.1)

3.2.3.   50 and 100 ml beakers

3.2.4.   100 ml separating funnel

3.2.5.   20 ml pipette

3.2.6.   Boiling regulators

3.3. Reagents

3.3.1.   Sulphuric acid (ρ = 1.85 g/ml)

3.3.2.   Sodium sulphate anhydrous

3.3.3.   Methanol, acidified
Into 1 l of a methanol 98-99 per cent (V/V), dissolve 10 g of sulphuric acid (3.3.1).

3.3.4.   Sulphuric acid, aqueous solution
Add 1 volume of sulphuric acid (3.3.1) to 4 volumes of distilled water.

3.3.5.   Sodium chloride, 100 g/l aqueous solution

3.3.6.   Potassium hydroxide, ethanolic solution
Dissolve 1.8 g of potassium hydroxide in about 2 ml of distilled water and dilute with 15 ml of 95 per cent (V/V) ethanol.

3.3.7.   Potassium hydroxide, 0.2 N ethanolic solution, accurately standardised

3.3.8.   Phenolphthalein 10 g/l solution into 95 per cent (V/V) ethanol

3.4. Procedure

3.4.1.   "Insoluble crude acids" preparation

Into a 50 ml round-bottomed flask (3.2.1), weigh about 5 g of the sample. Add the whole of the potassium hydroxide ethanolic solution (3.3.6) and a boiling regulator (3.2.6). Fit a

reflux condenser (3.2.2). Gently heat until boiling while shaking the mixture. Maintain gentle boiling for 1 hour.
Distil the greater part of the ethanol (about 13 ml) avoiding drying of the soap.
Add about 25 ml of boiling water and mix to dissolve the soap. Transfer the soap solution into a 100 ml beaker (3.2.3), add 50 ml of boiling water and bring to the boil for 45 minutes in order to eliminate the rest of ethanol.
Make up the contents of the beaker to about 70 ml with water. Transfer the soap solution to a 100 ml round-bottomed flask (3.2.1). Add cautiously 7 ml of sulphuric acid aqueous solution (3.3.4) and a boiling regulator (3.2.6). Fit a reflux condenser (3.2.2) and bring to the boil. Maintain boiling until the "total crude acids" float as a clear layer. Transfer the contents of the round-bottomed flask to a separating funnel (3.2.4) and draw off as completely as possible the aqueous layer. Wash the "insoluble crude acids" twice, each time with about 50 ml of the sodium chloride aqueous solution (3.3.5) eliminating each time the aqueous layer as completely as possible. Transfer the "insoluble crude acids" to a 50 ml beaker (3.2.3). Add a little anhydrous sodium sulphate (4.3.3), shake and filter through a dry filter paper. Allow the "insoluble crude acids" to crystallize for 24 hours in a desiccator.

3.4.2. Preparation of the methyl esters and titration of the free acidity

Weigh, to the nearest 0.01 g, about 2 g of "insoluble crude acids" into a 250 ml round-bottomed flask (3.2.1). With a pipette (3.2.5), add 20 ml of the acidified methanol (3.3.3) and a boiling regulator (3.2.6). Fit the reflux condenser (3.2.2). Allow to boil gently. Allow to cool to room temperature.
Add 2 or 3 drops of the phenolphthalein solution (3.3.8). Titrate the free acidity with the potassium hydroxide solution (3.3.7). At the same time carry out a blank test.

3.5. Expression of results

The rosin content, as a percentage (m/m), is given by the formula :

$$1.014 \times \left(\frac{33 \times T \times (V_1 - V_2)}{m} - 1.4 \right) \text{ (Notes 2 and 3)}$$

where :

V_1 is the number of ml of the potassium hydroxide solution used for the test

V_2 is the number of ml of the potassium hydroxide solution (3.3.7) used for the blank test

T is the exact normality of the potassium hydroxide solution (3.3.7) used

m is the mass, in g, of the test portion

4. POTENTIOMETRIC METHOD

4.1. Principle

Preparation of the "insoluble crude acids". Transformation to their methyl esters the nonrosin acids contained in the "insoluble crude acids".
Preparation of the methyl esters of the fatty acids of a check sample having the same mass as the test portion but free from rosin acids. In both cases, controled titration with a pH meter of the free acidity after treatment.
By subtraction and further calculations determination of the rosin content. (Note 4).

4.2. Apparatus

4.2.1. 100 ml and 250 ml round-bottomed flasks

4.2.2. Reflux condensers to fit flasks (4.2.1)

4.2.3. 100 ml and 250 ml beakers

4.2.4. 250 ml separating funnel

4.2.5. 5 ml and 50 ml pipettes

4.2.6. Stirrer, preferably a magnetic stirrer

4.2.7. Boiling regulators

4.2.8. pH meter with a glass electrode

4.3. Reagents

4.3.1. Methanol, 98-99 per cent (V/V)

4.3.2. Sulphuric acid (ρ = 1.85 g/ml)

4.3.3. Sodium sulphate anhydrous

4.3.4. Methanol acidified
Into 1 l of methanol (4.3.1) dissolve 10 g of sulphuric acid (4.3.2).

4.3.5. Sulphuric acid, aqueous solution
Add 1 volume of sulphuric acid (4.3.2) to 4 volumes of distilled water.

4.3.6. Sodium chloride, 100 g/l aqueous solution

4.3.7. Potassium hydroxide, ethanolic solution
Dissolve 3.6 g of potassium hydroxide into about 4 ml of distilled water and dilute with 30 ml of ethanol 95 per cent (V/V).

4.3.8. Potassium hydroxide, 0.2 N ethanolic solution, accurately standardised

4.4. Procedure

4.4.1. "Insoluble crude acids" preparation

Into a 100 ml round-bottomed flask (4.2.1) weigh about 10 g of the sample. Add the whole of the ethanolic potassium hydroxide solution (4.3.7) and a boiling regulator (4.2.7). Fit a reflux condenser (4.2.2). Gently heat until boiling while shaking the mixture. Maintain gentle boiling for 1 hour.
Distil the greater part of the ethanol (about 25 ml) avoiding drying of the soap.
Add about 50 ml of boiling water and mix to dissolve the soap. Transfer the soap solution into a 250 ml beaker (4.2.3), add 100 ml of boiling water and bring to the boil for 45 minutes in order to eliminate the remaining ethanol.
Dilute the contents of the beaker to about 140 ml with water. Transfer the soap solution to a 250 ml round-bottomed flask (4.2.1) and add cautiously 14 ml of the aqueous sulphuric acid solution (4.3.5) and a boiling regulator (4.2.7). Fit a reflux condenser (4.2.2) and bring to the boil. Maintain boiling until the "insoluble crude acids" overfloat in a clear layer.
Transfer the contents of the round-bottomed flask to a separating funnel (4.2.4) and draw off the aqueous layer as completely as possible. Wash the "insoluble crude acids" twice, each time with about 100 ml of the sodium chloride aqueous solution (4.3.6) eliminating each time the aqueous layer as completely as possible. Transfer the "insoluble crude acids" to a 100 ml beaker (4.2.3). Add a little anhydrous sodium sulphate (4.3.2), shake, and filter through a dry filter paper. Allow the insoluble fatty acids to crystallize for 24 hours in a desiccator.

4.4.2. Esterification - titration

Weigh to the nearest 0.01 g, about 4 g of "insoluble crude acids" into a 100 ml round-bottomed flask (4.2.1). With a pipette (4.2.5) add 50 ml of acidified methanol (4.3.7).
Fit a reflux condenser (4.2.2). Bring to gentle boiling for 30 minutes.
Allow to cool to room temperature.
Transfer quantitatively to a 100 ml beaker (4.2.3) by using three 5 ml portions of methanol (4.3.3) added with a pipette (4.2.5). Place the electrode of the pH meter (4.2.8) into the beaker. Start stirring with the stirrer (4.2.6). Titrate with the potassium hydroxide solution (4.3.8) between the two inflection points which are identical in practice to two inflection points of the neutralisation curve (corresponding generally to the graduations 4 and 10 of the pH scale of an instrument calibrated with water). Under the same conditions carry out a blank test with an equal mass of fatty acids free from oxidized acids. (Note 4).

4.5. Expression of results

The rosin content, expressed as a percentage (m/m), is given by the formula :

$$\frac{33 \times T \times (V_1 - V_2)}{m} \quad \text{(Note 3)}$$

where :

V_1 is the number of ml of the potassium hydroxide solution (4.3.8) used for the test

V_2 is the number of ml of the potassium hydroxide solution (4.3.8) used for the blank test

T is the exact normality of the potassium hydroxide solution (4.3.8) used

m is the mass, in g, of the test portion

5. NOTES

1. The determination of the rosin content is approximate as the molecular mass of the constituent rosin acids is unknown, and as oxidized acids may be present.

2. The correction factors are introduced in order to take into consideration the esterification limit of the fatty acids.

3. In the formula, the mean molecular mass of the rosin acids is considered be equal to 330. It should be replaced by the exact mean molecular mass when it is known.

4. The blank test is necessary to take into consideration the acid impurities contained in the methanol, and the incomplete esterification of the nonrosin fatty acids. It is thus desirable to use a fatty acids mixture whose composition is as close as possible to the composition of the fatty acids under examination. When the precise nature of the fatty acids present is not known, use a mixture of equal parts of coconut oil fatty acids, stearic acid and oleic acid.

IV. ALKALINE SOAPS   1982

4.213 DETERMINATION OF THE UNSAPONIFIED SAPONIFIABLE + UNSAPONIFIABLE
MATTER CONTENT, OF THE UNSAPONIFIABLE MATTER CONTENT, AND OF THE
UNSAPONIFIED SAPONIFIABLE MATTER CONTENT

(Fifth Edition : Method IV.A.11)

1. SCOPE

This Standard describes a method for the determination of the unsaponified saponifiable +
unsaponifiable matter content, of the unsaponifiable matter content, and of the unsaponified
saponifiable matter content in commercial soaps, excluding compounded products.

2. FIELD OF APPLICATION

This Standard is not applicable to soaps enriched with sterols or long chain alcohols, nor
to soaps containing perfume.

3. DEFINITION

The unsaponified saponifiable + unsaponifiable matter content is the quantity, expressed as
a percentage (m/m), of matter soluble in hexane,other than free fatty acids, which is not
saponified or is unsaponifiable.
The unsaponifiable matter content is the quantity, expressed as a percentage (m/m), of
matter soluble in hexane, other than the free fatty acids which is not saponified under
the conditions of the present method.
The unsaponified saponifiable matter is the quantity, expressed as a percentage (m/m), of
matter soluble in hexane, other than the free fatty acids which is non-saponified in the
soap but saponified under the conditions described in the present method.

4. PRINCIPLE

Extraction of matter soluble in hexane. Determination of the extracted mass. Determination
of the free fatty acids mass contained in the extract by titration with a potassium hydro-
xide solution. By subtraction, calculation of the unsaponified saponifiable + unsaponifiable
mass.
Saponification of the extract. Extraction of the non-saponifiable, hexane soluble matter.
Determination of the extracted mass which represents the mass of unsaponifiable matter.
By subtraction, calculation of the unsaponified saponifiable mass.

5. APPARATUS

5.1. 250 ml beaker

5.2. 50 ml, 250 ml round-bottomed flasks

5.3. Reflux condenser to fit 250 ml round-bottomed flasks (5.2)

5.4. 50 ml, 250 ml separating funnels

5.5. Microburette, 2 ml

5.6. Oven, regulated at 103 $\pm$ 2°C

6. REAGENTS

6.1. n-Hexane or, failing this, petroleum ether, b.p.= 40 – 60°C, bromine number less than
1, and free from residue

6.2. Ethanol, 50 per cent (V/V) aqueous solution

6.3. Ethanol, 95 per cent (V/V), neutralised with the potassium hydroxide solution (6.6)
in the presence of phenolphthalein (6.7)

6.4. Sodium hydrogen carbonate, 10 g/l aqueous solution

6.5. Potassium hydroxide, about 2 N ethanolic solution

6.6. Potassium hydroxide, 0.1 N ethanolic solution accurately standardised

6.7. Phenolphthalein, 10 g/l solution in 95 per cent (V/V) ethanol

7. PROCEDURE

7.1. Determination of the unsaponified saponifiable + unsaponifiable matter

Weigh, to the nearest 0.01 g into a beaker (5.1), about 5 g of finely grated soap. Add
about 55 ml of ethanol (6.3) and about 45 ml of the sodium hydrogen carbonate solution
(6.4). Heat to a temperature not exceeding 70°C.
After complete dissolution, allow to cool to room temperature.
Transfer quantitatively to a 250 ml separating funnel (5.4). Wash the beaker several times
with an equal volumes mixture of ethanol (6.3) and of the sodium hydrogen carbonate solution
(6.4). Extract 3 times using each time about 50 ml of hexane (6.1). Combine quantitatively
the 3 extracts. Filter if impurities are suspended. Wash the extract 3 times with, each
time, about 50 ml of an equal volumes mixture of ethanol (6.3) and distilled water. Dry
and tare a 250 ml round-bottomed flask (5.2). Transfer the extracts to this round-bottom-
ed flask (5.2). Evapore the greater part of the hexane (6.1).
Dry the residue in the oven (5.6) until a constant mass is obtained. (Note 1).
Dissolve the residue with a few millilitres of the ethanol (6.3). Add 3 drops of phenolph-
thalein (6.7). By means of a microburette (5.5), titrate the free acidity with the potas-
sium hydroxide solution (6.6) until a pink colour is obtained.

7.2. Determination of the unsaponifiable matter

Continue by adding 10 ml of the potassium hydroxide solution (6.6). Connect the reflux
condenser (5.3). Heat to gentle boiling for 30 minutes.
Add down the condenser about 10 ml of distilled water. Shake. Transfer to a 50 ml sepa-
rating funnel. Rinse the round-bottomed flask several times with a few millilitres of the
ethanol (6.3). Extract 3 times, each time with about 10 ml of hexane (6.1). Dry and tare
a 50 ml round-bottomed flask (5.2). Transfer quantitatively the extracts to the 50 ml
tared round-bottomed flask (5.2). Evaporate the greater part of the hexane (6.1).
Dry the residue in the oven (5.6) until a constant mass is obtained. (Note 1).

8. EXPRESSION OF RESULTS

The unsaponified saponifiable + unsaponifiable matter content, expressed as a percentage
(m/m), is given by the formula :

$$(m_1 - \frac{V \times M \times T}{1000}) \times \frac{100}{m}$$

The unsaponifiable matter content, expressed as a percentage (m/m), is given by the formula :

$$m_2 \times \frac{100}{m}$$

The unsaponified saponifiable matter content, expressed as a percentage (m/m), is given by
the formula :

$$(m_1 - \frac{V \times M \times T}{1000} - m_2) \times \frac{100}{m}$$

where :

> V is the number of ml of the standardised potassium hydroxide solution (6.6) used to
> neutralise the free fatty acids contained in the hexane soluble matter
>
> T is the exact normality of the standardised potassium hydroxide solution (6.6) used
>
> m is the mass, in g, of the test portion
>
> m_1 is the mass, in g, of the dry residue representing the unsaponified saponifiable+
> unsaponifiable matter
>
> m_2 is the mass, in g, of the dry residue representing the unsaponifiable matter
>
> M is the mean molecular mass, in g, of the fatty acids of the soap. (Note 2)

9. NOTES

1. In order to obtain a "constant mass", the residue should be dried rapidly at 103 $\pm$ 2°C, until the difference between two successive weighings, separated by a period in the oven of 5 minutes does not exceed 2 mg.

2. The mean molecular mass M of the fatty acids of the soap can be determined by titration of the fatty acids isolated after complete saponification of the sample, the elimination of the unsaponifiable matter and the acidification of the soap solution.

IV. ALKALINE SOAPS   1982

4.301 DETERMINATION OF THE FREE GLYCEROL CONTENT

(TITRIMETRIC METHOD)

(Fifth Edition : Method IV.A.10)

1. SCOPE

This Standard describes a method for the determination of the free glycerol content of commercial soaps excluding compounded products.

2. FIELD OF APPLICATION

This Standard is not applicable in the presence of organic compounds containing more than two hydroxyl groups on adjacent carbon atoms.
For soaps with low free glycerol content (less than 0.5 per cent), method 4.302 should be used.

3. DEFINITION

The free glycerol content is the quantity of glycerol expressed as a percentage (m/m) and determined by the present method.

4. PRINCIPLE

Decomposition of the soap by sulphuric acid followed by extraction of the fatty acids. Oxidation of the glycerol by sodium metaperiodate in the presence of a strong acid. Titration of the formic acid (produced during the reaction) with a standardised sodium hydroxide solution, using a pH meter.

5. REACTION

$$CH_2OH-CHOH-CH_2OH + 2\ NaIO_4 \longrightarrow HCOOH + 2\ HCOH + 2\ NaIO_3 + H_2O$$

6. APPARATUS

Cork stoppers should not be used and glass apparatus with ground-glass joints are recommended.

6.1.   150 ml and 250 ml beakers

6.2.   600 ml tall form beaker

6.3.   500 ml conical flask

6.4.   250 ml separating funnels

6.5.   5 ml graduated pipette

6.6.   50 ml burette with a fine jet to deliver 30 drops per ml

6.7.   250 ml volumetric flasks

6.8.   1000 ml volumetric flask

6.9.   Stirrer, preferably a magnetic stirrer
       In this case check that it does not influence the pH meter

6.10. pH meter, with a glass electrode. (Note 1)

6.11. Lens suitable for reading the burette to the nearest 0.02 ml

6.12. Watch glass

7. REAGENTS

7.1.   Distilled water or water of equivalent purity, freed from carbon dioxide by boiling for 15 minutes and cooling in a flask protected against atmospheric carbon dioxide

7.2. Diethyl ether, recently distilled. (Note 2)

7.3. Ethylene glycol (1,2-Ethanediol), free from glycerol, solution in distilled water
(7.1) 1 : 1 (V/V)

7.4. Sulphuric acid, aqueous solution, approximately 7 N

7.5. Sulphuric acid, aqueous solution, approximately 0.1 N

7.6. Sodium hydroxide, aqueous solution, approximately 2 N

7.7. Sodium hydroxide, aqueous solution, approximately 0.05 N

7.8. Sodium metaperiodate ($NaIO_4$), neutral, titre at least 98 per cent (m/m), aqueous
acid solution 60 g/l. (Note 3)

7.9. Sodium hydroxide, 0.1 N aqueous solution, accurately standardised

7.10. Sodium hydroxide, 0.125 N aqueous solution, accurately standardised, and free from
carbon dioxide. (Note 4)

7.11. Potassium hydrogen phthalate $C_6H_4(COOK)(COOH)$, 0.05 M aqueous solution (10.12 g/l,
pH 4.00 at 20°C). (Note 5)

7.12. Disodium tetraborate decahydrate ($Na_2B_4O_7$, 10 H_2O), 0.01 M aqueous solution (3.81 g/l,
pH 9.22 at 20°C). (Note 5)

7.13. Phenol red

8. PROCEDURE

8.1. Fatty acids extraction

In a beaker (6.1) weigh, to the nearest 0.01 g, about 10 g of soap. Dissolve with 100 ml
warm distilled water and when completely dissolved, transfer the solution quantitatively
to a separating funnel (6.4). Add about 10 ml sulphuric acid (7.4). Mix. Allow to cool.
Add about 100 ml diethyl ether (7.2). (Note 2). Mix. Allow to stand.
Draw off the aqueous layer into a second separating funnel (6.4). Add about 50 ml diethyl
ether (7.2). Mix. Allow to stand.
Draw off the aqueous layer into a third separating funnel (6.4). Add about 50 ml diethyl
ether (7.2). Mix. Allow to stand.
Draw off the aqueous acid into a volumetric flask (6.7). Combine the ethereal extracts.
Wash these extracts twice with about 50 ml distilled water (7.1). Combine the washing
waters and the acid water in the volumetric flask (6.7). Dilute to 250 ml with distilled
water (7.1).

8.2. Glycerol determination

Take a volume of the test portion in accordance with the following table. (Note 6).

Expected glycerol content of the sample, as a percentage (m/m)	Volume of the solution to be taken for the determination, in ml
16 to 20	50
12 to 16	75
8 to 12	100
6 to 8	150
4 to 6	200
less than 4	250

Pour the test portion into a beaker (6.2). Insert the glass electrode. Start stirring
by means of the stirrer (6.9). Whenever the pH is less than 3, add drop by drop, the
sodium hydroxide solution (7.7) until the pH reaches 3. Then add, drop by drop, the sodium
hydroxide solution until the pH reaches 8.1 + 0.1. With a pipette (6.5), add 50 ml of
the sodium metaperiodate solution (7.8). Cover with a watch glass (6.12) and allow to
stand for 30 minutes in the dark at room temperature (below 35°C).
Add 10 ml of ethylene glycol (7.3). Mix thoroughly. Cover with a watch glass (6.12) and
allow to stand for 2 minutes in the dark at room temperature (below 35°C).
By means of the burette (6.6), titrate with the sodium hydroxide solution (7.10) until
pH 8.1 + 0.1, using the pH meter (6.10). Note to the nearest 0.02 ml, by means of the
lens (6.11), the number of ml of the sodium hydroxide solution (7.10) used.

8.3. Blank test

Into a 250 ml beaker (6.1), introduce about 10 ml of sulphuric acid (7.4). Add about
200 ml of distilled water (7.1). Mix. Allow to cool.
Add a few drops of diethyl ether (7.2) in order to saturate the solution. Mix well. Take
a volume equal to that of the test portion and continue as indicated for the test portion,
except for the final titration (using the pH meter) which should be stopped at pH 6.5
± 0.1.

9. EXPRESSION OF RESULTS

The free glycerol content is given by the formula :

$$(V_1 - V_2) \times T \times 0.0921 \times \frac{250}{V_0} \times \frac{100}{m}$$

where :

V_0 is the number of ml of the acid solution taken in the glycerol determination

V_1 is the number of ml of the sodium hydroxide solution (7.10) used in the
glycerol determination

V_2 is the number of ml of the sodium hydroxide solution (7.10) used in the blank
test

T is the exact normality of the sodium hydroxide solution (7.10)

m is the mass, in g, of the test portion

10. NOTES

1. The pH meter should be checked with 2 buffer solutions (7.11 and 7.12).

2. In the absence of oxidised fatty acids, the diethyl ether should be replaced by
petroleum ether (b.p. = 30-50°C).

3. Sodium metaperiodate

3.1. Check of the sodium metaperiodate neutrality

In a conical flask (6.3), dissolve 5 g of sodium metaperiodate (7.8) with 150 ml of
distilled water (7.1). Add 5 ml of ethylene glycol (7.3). Allow to stand in the
dark protected from atmospheric carbon dioxide for 30 minutes.
Under these conditions, the solution should be neutralised in the presence of phenol
red (7.13) with a few drops of sodium hydroxide (7.9), which should amount to less
than 1 ml and preferably less than 0.2 ml.

3.2. Preparation of the acid solution

Weigh, to the nearest 0.1 g, 60 g of sodium metaperiodate (7.8). Dissolve in the
cold state with a solution of 120 ml of sulphuric acid (7.5) diluted in 500 ml of
distilled water (7.1). Transfer to a volumetric flask (6.8), dilute to 1000 ml with
distilled water (7.1) and mix thoroughly. If necessary, filter through a glass filter.

3.3. Check of the acid solution acidity

The number of ml of the sodium hydroxide solution (7.10) used for the blank test (8.3)
should not less than 4.5 ml.

3.4. Storage of the acid solution

Store the solution in a dark glass flask, fitted with a ground-glass stopper.

4. Until a primary standard is established internationally, it is recommended that the
standardisation of the solution (7.8) be carried out by means of the same batch of
primary standard.

5. Use standard materials specially prepared for pH measurements.

6. In order to determine the glycerol under the best conditions of operation with 50 ml
of sodium metaperiodate (7.8), it is necessary that the test portion used for the
determination contain 0.3 to 0.5 g of glycerol. Whenever the test portion is too
small, results will be expressed with an error by excess and less accurate. Whenever
the test portion is too high, results will be expressed with an error by defect. When-
ever the result obtained does not fall within the prescribed limits, repeat the deter-
mination with an adjusted test portion.

IV. ALKALINE SOAPS   1982

4.302   DETERMINATION OF LOW FREE GLYCEROL CONTENT
(SPECTROPHOTOMETRIC METHOD)
(Fifth Edition : Method IV.A.12)

1.   SCOPE

This Standard describes a method for the determination of minor quantities of free glycerol in soaps.

2.   FIELD OF APPLICATION

This Standard is applicable to commercial soaps, excluding compounded products, having a low free glycerol content.

3.   DEFINITION

The low free glycerol content is the quantity of free glycerol, less than 0.5 per cent, expressed as a percentage (m/m), and determined by the present method.

4.   PRINCIPLE

Decomposition of the soap by sulphuric acid followed by extraction of the fatty acids with petroleum ether.
Oxidation of the free glycerol remaining in the aqueous phase by periodic acid to formic acid and formaldehyde.
After reaction with chromotropic acid, the aldehyde formed gives a coloration whose intensity is proportional to the free glycerol content.

5.   APPARATUS

5.1.   250 ml round-bottomed flask

5.2.   50 ml conical flask with ground-glass stopper

5.3.   250 ml separating funnel

5.4.   100 ml, 250 ml and 1000 ml volumetric flasks

5.5.   1 ml, 2 ml, 10 ml, 50 ml graduated pipettes

5.6.   Burettes, 5 ml, graduated in 0.1 ml

5.7.   Spectrophotometer

5.8.   Cells, path-length 1 cm, suitable for (5.7)

5.9.   Water bath

6.   REAGENTS

6.1.   Petroleum ether, b.p. = 40-60°C, free from residue

6.2.   Hydrochloric acid (ρ = 1.18 g/ml)

6.3.   Sulphuric acid, 0.5 N aqueous solution

6.4.   Sulphuric acid, 200 g/l (about 4.6 N) aqueous solution (ρ = 1.14 g/ml)

6.5.   Sulphuric acid, 640 g/l (about 20 N) aqueous solution (ρ = 1.54 g/ml)

6.6.   Sulphuric acid, 836 g/l (about 30 N) aqueous solution

6.7.   Chromotropic acid, solution prepared as follows :
    Weigh, either 0.25 g of the hydrated disodium salt, or 0.23 g of the anhydrous disodium salt of 1,8-dihydroxynaphthalene-3,6-disulphonic acid, purity not less than 99 per cent, into a 250 ml volumetric flask (5.4). Dissolve in 10 ml water. Dilute to the mark with sulphuric acid (6.5). If necessary filter the solution through a sintered glass filter. The reagent should be kept in the dark. It may be used until

the transmittance in a cell (5.8) is not lower than 75 per cent at a wavelength equal to 571 nm.

6.8. Stannous chloride, aqueous solution prepared as follows :
Weigh 3.0 g of hydrated stannous (II) chloride ($SnCl_2$, $2H_2O$) into a 100 ml volumetric flask (5.4) and dissolve with 3 ml of hydrochloric acid (6.2). Dilute to the mark with distilled water. The reagent shall be freshly prepared.

6.9. Sodium metaperiodate, solution about 0.03 M prepared as follows :
Weigh 1.6 g of sodium metaperiodate ($NaIO_4$), purity not less than 99.8 per cent, into a 250 ml volumetric flask (5.4). Dissolve with about 100 ml sulphuric acid (6.3). Dilute to the mark with this sulphuric acid.

6.10. Glycerol, concentration determined according to method 3.121

6.11. Glycerol, standard solution prepared as follows :
Weigh an amount of glycerol (6.10) corresponding to 500.0 mg of pure glycerol. Transfer quantitatively to a 1000 ml volumetric flask (5.4). Dilute to the mark with distilled water. Mix thoroughly. Transfer by pipette 50 ml of this solution to another 1000 ml volumetric flask (5.4). Mix thoroughly and dilute to the mark with distilled water; 1 ml of this solution contains 25 µg of glycerol.

7. PROCEDURE

7.1. Construction of the calibration graph

To individual 100 ml volumetric flasks (5.4), transfer by means of a 5 ml burette (5.6) : 0.40 ml, 0.80 ml, 1.40 ml and 2.00 ml of the glycerol standard solution, containing respectively 10 µg, 20 µg, 35 µg and 50 µg of glycerol. Add to each flask distilled water until the total volume is equal to 2 ml. Add by pipette 1 ml of the metaperiodate solution (6.4). Allow to stand for 15 minutes.
By means of pipettes (5.5), add 1 ml of the stannous chloride solution (6.8) and 10 ml of the chromotropic acid solution (6.7). Mix thoroughly. Heat the flasks for 30 minutes on a boiling water bath (5.9).
Allow to cool to room temperature.
Dilute the contents of each flask to the mark with the sulphuric acid solution (6.5). Mix thoroughly (solution S_1). Fill a cell (5.8) with one of the solutions S_1. By means of the spectrophotometer (5.7), measure the absorbance at a constant temperature between 15 and 25°C and at the wavelength close to 571 nm which corresponds to the maximum absorption. (Note 1). Plot the calibration curve with the mass, in µg, of glycerol contained in each of the solutions S_1, as abscissae, and the corresponding absorbance values as ordinates.

7.2. Blank test

Add 2 ml of distilled water to a 100 ml volumetric flask (5.4). Follow the procedure as indicated in 7.1 from "Add by pipette 1 ml of the metaperiodate solution ..." until "... to the maximum absorption. (Note 1).".

7.3. Determination

The amount of the test portion should be determined from the following table :

Maximum expected content of glycerol, expressed as a percentage (m/m)	Maximum mass of the test portion, in g
0.500	0.5
0.250	1.0
0.125	2.0
0.080 or less	3.0

Weigh the test portion, to the nearest 0.001 g, into a conical flask (5.2) fitted with a ground-glass stopper. Add 20 ml of the sulphuric acid solution (6.4) and warm on the water bath (5.9) until the fatty acids form a clear layer. Transfer the mixture to a 250 ml separating funnel (5.3) rinsing the conical flask twice with 25 ml of petroleum ether (6.1) and then with 25 ml of distilled water. Allow to stand.
Draw off the aqueous layer into a round-bottomed flask (5.1). Extract the ethereal phase twice, each time with 10 ml of distilled water. Combine the washing liquids with the first aqueous phase. Remove the petroleum ether present in this mixture by warming the flask on the water bath (5.9). Cool.
Transfer the solution to a 100 ml volumetric flask (5.4). Dilute to the mark with distilled water. Mix thoroughly (solution S). (Note 2). Transfer by pipette 2 ml of solution S to a 100 ml volumetric flask (5.4). Follow the procedure as indicated in 7.1 from "Add by

pipette 1 ml of the metaperiodate solution ..." until "... to the maximum absorption. (Note 1).". Subtract the blank test absorbance (7.2). Read on the calibration graph (7.1) the mass, in μg, of the glycerol contained in the coloured solution.

8. EXPRESSION OF RESULTS

The free glycerol content, expressed as a percentage (m/m), is given by the formula :

$$0.005 \ x \frac{m_1}{m}$$

where :

   m is the mass, in g, of the test portion

   m_1 is the mass, in μg, contained in the coloured solution and read from the calibration curve

9. NOTES

1. The exact wavelength corresponding to maximum absorption should be determined for the particular spectrophotometer used.

2. Whenever the solution S is turbid (due to the fact that titanium oxide may be present) transfer it to a 100 ml volumetric flask (5.4) filtering it through a filter paper. Dilute to the mark by washing the filter several times with distilled water.

IV. ALKALINE SOAPS   1982

4.311 DETERMINATION OF MOISTURE AND VOLATILE MATTER CONTENT
(OVEN METHOD)
(Fifth Edition : Method IV.A.2)

1. SCOPE AND FIELD OF APPLICATION

This Standard describes a method for the determination of the moisture and volatile matter content, removed by heating at 103 $\pm$ 2°C and contained in commercial soaps excluding compounded products.

2. DEFINITION

The moisture and volatile matter content of soaps is the quantity of water and volatile matter determined by the present method and expressed as a percentage (m/m).

3. PRINCIPLE

Evaporation of the water and the volatile matter contained in a test portion by heating at 103°C.

4. APPARATUS

4.1. Porcelain or glass evaporating dish, 8 to 9 cm diameter and 4 to 5 cm deep, containing a stirring rod. (Note 1)

4.2. Desiccator containing an efficient desiccant

4.3. Oven regulated at 103 $\pm$ 2°C

5. PROCEDURE

Dry the evaporating dish (4.1) and its eventual contents in the oven (4.3) regulated at 103 $\pm$ 2°C.
Allow to cool in the desiccator (4.2).
Tare. Place in the evaporating dish about 10 g of soap, weighed to the nearest 0.01 g, and eventually incorporate sand or pumice with the assistance of the stirring rod. (Note 1).
Replace in the oven (4.3) for 1 hour.
Allow to cool in the desiccator (4.2).
Weigh. Repeat successive weighings at 1 hour intervals until the mass difference observed between two successive weighings is less than 0.01 g. The last weighing gives the mass of the dried test portion.

6. EXPRESSION OF RESULTS

The moisture and volatile matter content, expressed as a percentage (m/m) is given by the formula :

$$\frac{100 \times (m_1 - m_2)}{m_1}$$

where :

m_1 is the mass, in g, of the test portion

m_2 is the mass, in g, of the dried test portion

7. NOTE

1. In the presence of liquid or soft soap liquefiable at 103°C, place into the evaporating dish about 10 g of washed and calcined sand or granulated pumice.

IV. ALKALINE SOAPS   1982

4.312 DETERMINATION OF THE WATER CONTENT
(AZEOTROPIC DISTILLATION METHOD)
(Fifth Edition : Method IV.A.2)

1. SCOPE

This Standard describes a method for the determination of the water content of commercial soaps excluding compounded products.

2. FIELD OF APPLICATION

This Standard is applicable to products in the form of powders having a water content greater than 5 per cent (m/m), and in the form of pastes and solutions. It is not applicable to samples containing water-soluble volatile compounds, for example ethanol.
With regard to soaps, as the results cannot be obtained with an accuracy greater than 0.3 per cent, this method should be used only for soaps containing appreciable amounts of volatile matter insoluble in water. This method is also recommended for soaps made with linseed oil or other drying oils and for certain soaps containing, for example, sodium silicate.

3. DEFINITION

The water content, expressed as a percentage (m/m), is the quantity of water distilled and collected following the method described.

4. PRINCIPLE

Azeotropic distillation, with boiling xylene, of the water contained in a test portion.

5. APPARATUS (Note 1)

5.1. Distillation apparatus comprising the following items :
5.1.1. Round-bottomed flask, of 500 ml minimum capacity, fitted with a ground glass joint.
5.1.2. Graduated collecting cylinders of capacity 2 or 10 ml (Dean-Stark receiver).
     The internal graduation and its tolerance for the 2 ml graduated collecting cylinder should be
     - graduation in 0.1 ml
     - maximum error : 0.05 ml
     The internal graduation and its tolerance for the 10 ml graduated collecting cylinder should be, after 1 ml :
     - graduation in 0.2 ml
     - maximum error 0.1 ml

5.2. Reflux condenser for connection to the collecting cylinders (5.1.2)

5.3. Boiling regulators, anhydrous

6. REAGENT

6.1. Xylene
     Any of the isomers or a mixture of these isomers in any proportion,b.p. : 130-140°C.

7. PROCEDURE

This procedure must be carried out in a fume cupboard to prevent exposure to toxic xylene vapors.
Into the round-bottomed flask (5.1.1) weigh, to the nearest 0.01 g, 10 to 50 g of the sample, the test portion being chosen so that the graduated collecting cylinder (5.1.2) is at least 50 per cent full at the end of the test. Add 100 to 300 ml of xylene (6.1) and boiling regulators (5.3). Connect the round-bottomed flask to the rest of the apparatus. Heat gradually to the boil and maintain boiling until the distilling xylene (2 to 3 drops per second) becomes clear and until there is no further separation of water. (Notes 2 and 3).

Allow to stand until the water is completely separated without an emulsified zone.
Read the volume of water in the graduated collecting cylinder, at the reference temperature of 20°C.

8. EXPRESSION OF RESULTS

The water content, expressed as a percentage (m/m), is given by the formula :

$$V \times \frac{100}{m}$$

where :

   V is the number of ml of the aqueous layer

   m is the mass, in g, of the test portion

9. NOTES

1. Before use, remove all traces of fatty matter from the graduated collecting cylinders and from the interior tube of the reflux condenser. Wash then successively with, for example, a proprietary detergent solution suitable for cleaning glassware, then with distilled water and finally with acetone. Dry. A perfect cleanliness of the apparatus is essential to the success of the test.

2. In the case of general and persistent foam, enclose the test portion in a dry filter paper or add to the round-bottomed flask, for example, dry paraffin or dry oleic acid.

3. If drops of water adhere to the wall of the graduated collecting tube, detach them during or after the distillation, for example, with a wire spiral washed with 5 ml of xylene.

IV. ALKALINE SOAPS   1982

4.313 DETERMINATION OF THE ETHANOL-INSOLUBLE MATTER CONTENT

(Fifth Edition : Method IV.A.3)

1. SCOPE

This Standard describes a method for the determination of the ethanol-insoluble matter content of commercial soaps.

2. FIELD OF APPLICATION

This Standard is applicable to commercial soaps excluding compounded products. It is suitable for the determination of foreign matter accompanying or added to soaps and which may belong to mineral substances such as carbonates, borates, perborates, chlorides, sulphates, silicates, phosphates, iron oxides, ..., or to organic substances such as starch, dextrin, caseins, sugars, cellulose derivatives, ...
It may be limited to the determination of added foreign matter or to a simple qualitative investigation.

3. DEFINITION

The ethanol-insoluble matter content is the quantity of foreign matter insoluble in absolute ethanol or in 95 per cent (V/V) ethanol, expressed as a percentage (m/m) and determined by the present method.

4. PRINCIPLE

Dissolution of the dried test portion in absolute boiling ethanol. Filtration and weighing of the insoluble matter.

5. APPARATUS

5.1. 500 ml conical flasks

5.2. Reflux condensers to fit flasks (5.1)

5.3. Evaporation dish with stirrer rod

5.4. Water bath

5.5. Oven regulated at 103 $\pm$ 2°C

6. REAGENTS

6.1. Ethanol, absolute, or for the determination of added chemical substances, or for qualitative investigation

6.2. Ethanol, 95 per cent (V/V)

7. PROCEDURE

7.1. Determination of the total foreign matter

Weigh, to the nearest 0.01 g, into the evaporation dish (5.3) about 5 g of soap. Place the evaporation dish into the oven (5.4) regulated at 103 $\pm$ 2°C for 1 hour, this ensures a sufficient desiccation.
Pound as far as possible with the stirrer. Transfer quantitatively to a conical flask (5.1). Add 200 ml of the ethanol (6.1). Connect the condenser (5.2) to the flask (5.1). Heat to gentle boiling with stirring in order to avoid as far as possible soap sticking to the bottom of the flask.
Dry a filter paper in the oven (5.5) regulated at 103 + 2°C.
Tare this filter paper. Place the tared filter paper in a funnel mounted on a conical flask (5.1).

Heat about 50 ml of ethanol (6.1) to near its boiling point. When the dissolution of the soap appears to be complete, transfer to the filter, after decantation, first the liquid then the insoluble matter with the aid of small quantities of the ethanol which has just been heated. (Note 1). Wash this insoluble matter with this ethanol until complete elimination of the soap. During this operation it is advantageous to place the flask carrying the funnel on a water bath (5.4) so as to keep the filtrate gently boiling and to cover the funnel with a watch glass, avoiding by this the cooling of the washing liquids. Furthermore the ethanol vapours condensed on the watch glass dropping upon the filter completes the washing. Dry the filter paper in the oven regulated at 103 $\pm$ 2°C for 1 hour.
Allow to cool in a desiccator. Weigh the dry filter. (Note 2).

7.2. Determination of the added foreign matter

Weigh, to the nearest 0.01 g, in a conical flask (5.1) about 5 g of soap. Add 200 ml of ethanol (6.2). Continue with the procedure as indicated in 7.1 : "Connect the condenser .. ." replacing, wherever necessary the ethanol (6.1) by the ethanol (6.2).

7.3. Qualitative analysis

Weigh about 5 g of soap in a conical flask (5.1). Add about 100 ml of the ethanol (6.2). Connect the condenser (5.2). Bring to gentle boiling until dissolution of the soap. The non dissolved portion is due to the presence of foreign matter in the soap. It should be noted that under the conditions of the method, substances present in any soaps (small quantities of carbonate and alkaline chloride) are soluble.

8. EXPRESSION OF RESULTS

The total or added ethanol-insoluble matter content is given by the formula :

$$\frac{100 \times m_2}{m_1}$$

where :

m_1 is the mass, in g, of the test portion

m_2 is the mass, in g, of the total residue obtained according to the appropriate method (7.1 or 7.2)

9. NOTES

1. With certain soaps, especially silicated soaps, the insoluble matter cannot be completely removed from the bottom of the conical flask. In this case, after thoroughly washing the residue with absolute ethanol, dissolve it in a few millilitres of warm distilled water.
   Tare a evaporation dish.
   Transfer the aqueous solution in the evaporating dish.
   Dry on the boiling water bath (5.4) and then in the oven regulated at 103 $\pm$ 2°C (5.5). Weigh the evaporation dish and determine the mass of the residue obtained.
   Add this mass to that of the dry filtered residue.

2. The residue collected on the filter may be used for the analysis of the carbonated alkalis and for the identification of the other total foreign substances.

IV. ALKALINE SOAPS   1982

4.321 DETERMINATION OF THE CHLORIDE CONTENT
(Fifth Edition : Method IV.A.8)

1. SCOPE AND FIELD OF APPLICATION

This Standard describes a method for the determination of the chloride content of commercial soaps, excluding compounded products.

2. DEFINITION

The chloride content is the quantity of sodium chloride or potassium chloride, expressed as a percentage by mass (m/m) and determined by the present method.

3. PRINCIPLE

Dissolving of the soap and precipitation of the chlorides by a known amount of silver nitrate. Determination of silver nitrate excess by ammonium thiocyanate. Calculation of the reacted quantity of silver nitrate and conversion to corresponding chloride.

4. APPARATUS

4.1. 100 ml beaker

4.2. 250 ml conical flask

4.3. 200 ml volumetric flask

4.4. Pipettes, 25 ml and 100 ml

4.5. Water bath

5. REAGENTS

5.1. Nitric acid (ρ = 1.32 g/ml)

5.2. Silver nitrate, 0.1 N aqueous solution, accurately standardised

5.3. Ammonium thiocyanate, 0.1 N aqueous solution, accurately standardised

5.4. Ammonium iron (III) sulphate (ferric alum), 100 g/l aqueous solution

6. PROCEDURE

Weigh, to the nearest 0.01 g, into the beaker (4.1) about 5 g of soap. Dissolve with 50 ml of distilled water. Transfer quantitatively to a flask (4.3) washing with small quantities of distilled water. Add 5 ml of nitric acid (5.1). Add immediately with a pipette (4.4), 25.0 ml of the silver nitrate solution (5.2). Place on the water bath (4.5) until the fatty acids are completely separated and the formed silver chloride gathers together. Cool to room temperature.
Dilute to 200 ml with distilled water and homogenise by shaking. Filter through a dry pleated filter. Discard the first 10 ml of the filtrate. Pipette 100 ml of the filtrate into the flask (4.2). Add 2 to 3 ml of ferric alum solution (5.4). Titrate with the ammonium thiocyanate solution (5.3) until the appearance of a reddish coloration.

7. EXPRESSION OF RESULTS

The chloride content is given by the following formulae :

- Content expressed as a percentage by mass (m/m) of sodium chloride :

$$\frac{5.85 \times \left[(25 \times T_1) - (2 \times V \times T_2)\right]}{m}$$

- Content expressed as a percentage by mass (m/m) of potassium chloride :

$$\frac{7.46 \times \left[(25 \times T_1) - (2 \times V \times T_2)\right]}{m}$$

where :

   V is the number of ml of the ammonium thiocyanate solution (5.3) used

   T_1 is the exact normality of the silver nitrate (5.2) used

   T_2 is the exact normality of ammonium thiocyanate solution (5.3) used

   m is the mass, in g, of the test portion

IV. ALKALINE SOAPS   1982
4.322   DETERMINATION OF THE CHLORIDE CONTENT
(POTENTIOMETRIC METHOD)

1. SCOPE

This Standard describes a potentiometric method for the determination of the chloride
content of commercial soaps.

2. FIELD OF APPLICATION

This Standard is applicable to commercial soaps containing, or not containing, other
surface active agents.

3. PRINCIPLE

Potentiometric titration of the Cl^- ions with a standard silver nitrate solution, in a
nitric acid medium, using a silver-silver chloride measurement electrode and a calomel
reference electrode.

4. DEFINITION

The chloride content of commercial soaps is the quantity, expressed as a percentage by mass
(m/m), of sodium chloride contained in soaps and determined by the present method.

5. APPARATUS

5.1.   200 ml beaker

5.2.   10 ml graduated pipette

5.3.   500 ml volumetric flask

5.4.   50 ml burette

5.5.   Electrodes
5.5.1.   Calomel electrode (potassium chloride saturated) (reference electrode)
5.5.2.   Silver-silver chloride electrode (measurement electrode)
or
5.5.3.   Combined electrode, as an alternative to electrode (5.5.1) and (5.5.2) and bridge
(5.6)

5.6.   Bridge
Liquid junction containing the saturated potassium nitrate solution (6.4), connected
to the calomel electrode (5.5.1).

5.7.   Potentiometer, sensitivity 2 mV (potential range -500 mV to +500 mV), preferably
equipped with a potentiograph which provides a more rapid and easier indication of
the equivalence point

5.8.   Electromagnetic stirrer

6. REAGENTS

6.1.   Nitric acid, approximately 6 N aqueous solution

6.2.   Potassium chloride, analytical reagent quality

6.3.   Silver nitrate, analytical reagent quality

6.4.   Potassium nitrate, aqueous solution, saturated at 20°C

6.5.   Silver nitrate, approximately 0.1 N standardised aqueous solution
Weigh 8.5 g of silver nitrate (6.3). Dissolve in a few millilitres of water and
transfer to a 500 ml volumetric flask (5.3). Make up to the mark. Mix.

6.6. Silver nitrate, approximately 0.01 N aqueous solution
      Prepare this solution immediately before use by appropriate dilution of the standar-
      dised solution (6.5).

6.7. Potassium chloride, 0.1 N standard reference aqueous solution
      Weigh, to the nearest 0.001 g, 3.728 g of potassium chloride (6.2) previously dried
      during 2 hours at 105°C and cooled in a drying oven.
      Dissolve in a few millilitres of water and transfer quantitatively the solution to
      a 500 ml volumetric flask (5.3). Make up to the mark. Mix.

6.8. Potassium chloride, 0.01 N standard reference aqueous solution
      Prepare this solution immediately before use by appropriate dilution of the standard
      reference solution (6.7).

6.9. Methyl orange, 1 g/l aqueous solution

7. PROCEDURE

7.1. Calibration of the silver nitrate solution

Before making any measurements, allow the potentiometer to operate for a sufficient time,
in order to obtain good electrical stabilisation.
Take care that the interior liquid of the calomel electrode (potassium chloride saturated)
(5.5.1) is in equilibrium with the atmospheric pressure, in order that its flow across the
bridge (5.6) is not obstructed. Note the temperature of the standard reference solution,
make the corresponding adjustments in the circuit for correction of temperatures, and
zero the apparatus. (Note 1). Do not alter the settings during the measurements.
With a pipette (5.2), introduce into a beaker (5.1) 10 ml of the standard reference
potassium chloride solution (6.7) or (6.8) according to whether the silver nitrate solution
to be standardised is 0.1 N or 0.01 N. Add 2 drops of methyl orange (6.9). Acidify
-several drops in excess- with the nitric acid (6.1). Add 100 ml water. Stir the resultant
solution. Immerse in this solution, either the combined electrode (5.5.3), or the silver-
silver chloride electrode (5.5.2) and the free end of the bridge (5.6). Connect the
electrodes (5.5.1 and 5.5.2) or the combined electrode to the potentiometer (5.7). By
means of a burette, add the silver nitrate solution to be standardised (6.5) or (6.6) until
the equivalence point is reached. Carry out this operation three times.
The normality of the used silver nitrate is given by the formula :

$$T = T_0 \times \frac{10}{V_m}$$

where :

V_m is the mean value of the silver nitrate volumes used for the three tests

T_0 is the normality of the potassium chloride reference solution used (6.7 or 6.8)

7.2. Titration

According to the expected chloride content, select the test portions and the reagent
solution as indicated in the following table :

Expected chloride content, expressed as NaCl per cent (m/m)	Mass of the test portion, in g	Normality of the silver nitrate solution used
Below 0.1	1 to 10	0.01 N
Above 0.1	1 to 3	0.1 N

Weigh, to the nearest 0.001 g, the appropriate test portion into a beaker (5.1). Add
100 ml hot water. Add 2 drops of the methyl orange solution (6.9). Acidify -several
drops in excess- with the nitric acid (6.1). Filter through a wet filter paper. Wash
the fatty acids retained on the paper with small portions of hot water. Allow the
filtrate to cool to room temperature.
From the burette (5.4) add the silver nitrate solution (6.5 or 6.6 corresponding to the
expected chloride content), until the equivalence point is reached.

8. EXPRESSION OF RESULTS

The chloride content, expressed as a percentage (m/m) of sodium chloride, is given by
the formula :

$$\frac{V \times T \times 0.0585 \times 100}{m}$$

where :

      V is the number of ml of silver nitrate (6.5 or 6.6) used to reach the equivalence point

      T is the normality of the silver nitrate solution used (6.5 or 6.6)

      m is the mass, in g, of the test portion

9. NOTE

1. In order to reduce the effects of thermal and electrical hysteresis, care should be taken that the temperatures of the electrodes, the water used for washings, the standard solutions and the test solution are as close to each other as possible. The temperatures of the standard solutions and the test solution should not differ by more than 1°C. The measurement temperature should be 20°C whenever possible.

IV. ALKALINE SOAPS   1982

4.331   DETERMINATION OF THE EDTA (sequestering agent) CONTENT
(TITRIMETRIC METHOD)

1. SCOPE

This Standard describes a titrimetric method for the determination of the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA) content in soaps.

2. FIELD OF APPLICATION

This method permits the determination of the disodium salt for contents higher than 0.1 per cent (m/m) in the presence of the trisodium salt of nitrilotriacetic acid (NTA). (Note 1).

3. DEFINITION

The EDTA content is the quantity of EDTA, expressed as its disodium salt as a percentage (m/m), contained in soaps and determined by the present method.

4. PRINCIPLE

Complexometric titration of the EDTA with a copper(II) sulphate solution in the presence of the monosodium salt of 4-(2-pyridylazo)resorcinol as indicator.

5. APPARATUS

5.1. 250 ml beaker

5.2. 100 ml conical flask

5.3. Graduated pipette of capacity adequate for taking from the S solution (see 7) an aliquot portion containing 0.003 to 0.005 g of EDTA

5.4. 500 and 1000 ml volumetric flasks

5.5. Microburette of capacity 2 ml

6. REAGENTS

6.1. Copper(II) sulphate pentahydrate ($CuSO_4$, 5 H_2O), minimum purity 99.5 per cent

6.2. Hydrochloric acid, approximately 5 N aqueous solution

6.3. Copper(II) sulphate, approximately 0.02 N aqueous standard solution
      Weigh, to the nearest 0.001 g, 2.497 g of copper(II) sulphate (6.1). Dissolve in distilled water. Transfer quantitatively the solution to a 1000 ml volumetric flask (5.4). Dilute to the mark. Mix.

6.4. 4-(2-pyridylazo)resorcinol (PAR), monosodium salt monohydrate, 1 g/l solution. (Note 2).

7. PROCEDURE

Weigh, to the nearest 0.001 g, into a beaker (5.1), about 10 g of the sample. Dissolve this test portion in approximately 200 ml of distilled water. Transfer quantitatively the solution obtained to a 500 ml volumetric flask (5.4). Dilute to the mark (solution S). By pipette (5.3) transfer to a conical flask (5.2) an aliquot portion of this solution containing 0.003 to 0.005 g of EDTA. Adjust the pH of the solution to between 4 to 5 by adding the hydrochloric acid solution (6.2). (Note 3). Add 4 drops of the PAR indicator (6.4). By means of the microburette (5.5) titrate with the copper sulphate solution (6.3) until the colour changes from yellow to red.

8. EXPRESSION OF RESULTS

The EDTA content, expressed as its disodium salt as a percentage (m/m), is given by the formula :

$$\frac{0.372 \times V_1 \times T \times 100 \times 500}{2 \times m \times V_0}$$

where :

V_0 is the number of ml of the aliquot portion taken for the determination

V_1 is the number of ml of the copper solution (6.3) used for the determination

T is the exact normality of the copper solution (6.3) used for the determination

m is the mass, in g, of the test portion

9. NOTES

1. In the presence of large amounts of NTA —more than 10 per cent (m/m)— interference may be produced.

2. If reagent PAR is not available, it is permitted to use the reagent PAN (1-(2-pyridylazo)-2-naphthol) provided that this is stated in the test report.

3. In most cases, there is no interference by other components of the sample, for example fatty acids, but if necessary, the fatty acids may be removed by filtration through a wet filter paper.