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METHODS OF ANALYSIS OF SOAPS

BUREAU OF CEYLON STANDARDS

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Ceylon Standards are subject to periodical revision in order to accommodate the progress made by industry. Suggestions for improvement will be recorded and brought to the notice of the committees to which the revisions are entrusted.

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CEYLON STANDARD METHODS OF ANALYSIS OF SOAPS

FOREWORD

This Ceylon Standard was prepared by the Drafting Committee on Soaps. It was approved by the Agricultural and Chemicals Divisional Committee of the Bureau of Ceylon Standards and was authorised for adoption and publication by the Council of the Bureau on 7th July, 1968.

In the preparation of this standard, considerable assistance was obtained from the publications of the British Standards Institution and the International Organisation for Standardization.

1. SCOPE

This Ceylon Standard describes methods of analysis of soaps and soap products.

It includes methods of analysis for the following types of soaps.

(i) Laundry soap, with or without added inorganic material such as sodium silicate, carbonate, phosphate and borate.

(ii) Toilet soaps.

(iii) Carbolic soaps.

(iv) Soap chips and flakes.

(v) Soap powders, ground or otherwise granulated, with or without the inorganic materials specified in (i) above.

2. PREPARATION OF SAMPLES FOR ANALYSIS

2.1 **Bars.** The bar shall be cut into eight parts by three cuts at right angles to each other, through the middle of the bar. Two diagonally opposite eighths of each bar shall be sliced finely. The slices shall be thoroughly mixed and placed in an air-tight container.

2.2 **Cakes or tablets.** The cakes or tablets shall be cut into halves along their longer axes. One half of each cake or tablet shall be sliced finely, mixed thoroughly and placed in an air-tight container.

2.3 **Soap powders.** The sample shall be mixed thoroughly, and all portions for analysis shall be weighed as soon as possible, preserving the remainder in an air-tight container. If the sample is lumpy, the lumps shall be broken down and thoroughly mixed with the remainder of the sample.

2.4 **Soft soaps.** The sample shall be mixed well by kneading and all portions weighed for analysis at one time, preserving the remainder in an air-tight container.

2.5 **All others.** Portions for analysis shall be taken direct from the well mixed sample.

3. DETERMINATION OF TOTAL FATTY MATTER

3.1 **Definition. Total fatty matter means the fatty material obtained by decomposing the soap with a strong mineral acid, and extracting the separated fatty matter with diethyl ether under the operating conditions described. This term includes unsaponifiable matter, glycerides and any resinic acids contained in the soap, in addition to the fatty acids derived from the soap.**

3.2 **Principle.** The fatty acids are extracted with diethyl ether and titrated with a solution of sodium hydroxide in ethanol and finally weighed as soap.

3.3 **Reagents.**

(i) Diethyl ether (pure).

(ii) Ethanol, 95 per cent (v/v).

(iii) Sulphuric acid, N solution.

(iv) Sodium chloride solution, 10g of sodium chloride dissolved in 100 ml of distilled water.

(v) Sodium hydroxide, (analytical grade) 0.5N ethanolic solution (recently standardized).

(vi) Methyl orange indicator, 0.2g in 100 ml of distilled water.

(vii) Phenolphthalein indicator, 1g in 100 ml of ethanol.

3.4 **Procedure.** Weigh, to the nearest milligramme, about 5g of soap and dissolve it in about 150 ml of hot distilled water in a beaker of about 200 ml capacity. Pour this hot, aqueous solution into a separating funnel rinsing the beaker with small quantities of hot distilled water. Add a few drops of the methyl orange and then from a burette add the acid solution so that there is an excess of about 5 ml. If the total alkali has also to be determined, note the exact quantity of acid added.

Add 100 ml of diethyl ether. Shake the mixture vigorously for one minute, and allow to stand until the two phases are completely separated.

Draw off the aqueous layer into a second separating funnel and re-extract with 50 ml of diethyl ether.

Draw off the aqueous layer. Combine the ether extracts in the first separating funnel. Wash with 50 ml portions of the sodium chloride solution, until the washings are neutral to methyl orange. Usually three washings are sufficient.

(*Note*. Reserve the aqueous solution and the washings. See Clause 4). Transfer the ethereal solution to a tared flask, filtering if necessary. Wash the filter with small portions of the diethyl ether. Distil off nearly all the diethyl ether by boiling gently.

Dissolve the residue in 20ml of the ethanol. Titrate the ethanolic solution of fatty acids with the ethanolic sodium hydroxide solution, using 2-3 drops of phenolphthalein as indicator. Note the volume used.*

Remove the ethanol by evaporation on a water-bath. Heat the flask in an oven at 120°C until the difference in weight, after drying in the oven for an additional 15 minutes does not exceed 5 mg. Note the weight of the dry soap (W_2).

3.5 **Calculation.** Total fatty matter, per cent by weight, in the soap

$$= [W_2 - (V \times 0.5 \times 0.022)] \times \frac{100}{W_1}$$

where W_1 = the weight in grammes of the test portion,

W_2 = the weight in grammes of dry soap

and V = the volume, in millilitres of ethanolic sodium hydroxide solution used.

Round off the result to the nearest 0.1 per cent.

Total fatty matter, per cent by weight, in the piece of soap, at time of receipt,

$$= [W_2 - (V \times 0.5 \times 0.222)] \times \frac{100}{W_1} \times \frac{W_4}{W_3}$$

where W_3 = the weight in grammes of the piece of soap at time of receipt

and W_4 = the weight in grammes of the piece of soap at the time of analysis.

*If the fatty acid colour masks the end-point, this may be determined potentiometrically.

4. DETERMINATION OF TOTAL ALKALI

4.1 Reagents.

(i) Sodium hydroxide, N solution.
(ii) Sulphuric acid, N solution.
(iii) Methyl orange indicator, 0.04 per cent (w/v) aqueous solution.

4.2 **Procedure.** Transfer the aqueous solution and the first three washings reserved under "Determination of total fatty matter" to a 350 ml conical beaker, distil off the ether on a water-bath, cool, add a measured excess of the sodium hydroxide solution, and titrate back with the sulphuric acid solution.

4.3 **Calculation.** Total alkali, per cent by weight, expressed as

$$Na_2O = 3.1 \frac{(V + V_2 - V_1)}{W}$$

where W = weight, in grammes, of test portion taken,
V = volume, in millilitres, of N sulphuric acid solution originally added to the soap solution,
V_1 = volume, in millilitres, of N sodium hydroxide solution added to the aqueous solution after removal of ether
and V_2 = volume, in millilitres, of N sulphuric acid solution required to neutralize the excess of N sodium hydroxide solution.

Alternatively, or if the total fatty matter is not determined, ignite about 10g of the sample of soap in a platinum basin. Thoroughly extract the charred residue by means of hot water, and after filtration, cool, and titrate the extract with the sulphuric acid solution, using methyl orange as indicator.

Total alkali, per cent by weight, expressed as $Na_2O = \frac{3.1V_3}{W}$

where V_3 = volume in millilitres of N sulphuric acid used
and W = weight in grammes of test portion taken.

5. DETERMINATION OF TOTAL FREE ALKALI

(for determination on toilet and unbuilt genuine soaps)

5.1 Reagents.

(i) Ethanol, 95 per cent (v/v).
(ii) Potassium hydroxide, 0.1 N ethanolic solution.
(iii) Sodium hydroxide, N solution.
(iv) Sulphuric acid, N solution.
(v) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.

5.2 **Procedure.** Boil 100 ml of ethanol in a 400 ml flask under reflux, add 0.5 ml of phenolphthalein indicator, allow to cool to 70°C and neutralize at that temperature with the ethanolic potassium hydroxide solution. Add 10 g of the sample in thin shavings and dissolve it as quickly as possibly by heating. Immediately after complete solution of the soap, add 3 ml of the sulphuric acid solution and boil on a water-bath for at least 10 minutes to ensure complete removal of carbon dioxide. If the solution is colourless, cool to 70°C and titrate back with the sodium hydroxide until the pink colour reappears. If, after boiling with acid, the pink colour returns, add a further quantity of the sulphuric acid solution and repeat the boiling, the titration being completed as described above. The excess of sulphuric acid solution finally titrated should be not less than 1 ml.

5.3 **Calculation.** Total free alkali, per cent by weight, expressed as

$$Na_2O = \frac{3.1\,(V_2 - V_1)}{W}$$

where W = weight in grammes of test portion taken,
V_1 = volume in millilitres of N sodium hydroxide solution required
and V_2 = volume in millilitres of N sulphuric acid solution added.

6. DETERMINATION OF FREE CAUSTIC ALKALI

6.1 Method 1

Method 1 (ethanol method) should be applied only to sodium soaps of ordinary quality.

6.1.1 Reagents

(i) Ethanol, absolute.
(ii) Potassium hydroxide, 0.1 N ethanolic solution.
(iii) Hydrochloric acid 0.1 N etanolic solution.
(iv) Phenolphthalein indicator, 1 g in 100 ml of 95 per cent ethanol (v/v).

6.1.2 Procedure. Weigh approximately 5 g of soap to an accuracy of 0.01 g.

Pour 200 ml of ethanol into a flask and connect to a reflux condenser. Bring to a gentle boil for 5 minutes, in order to remove carbon dioxide. Allow to cool to about 70°C. Add 4 drops of phenolphthalein indicator, neutralize exactly with the ethanolic solution of potassium hydroxide, until the indicator just turns pink.

Place the test portion in the flask containing the neutralized ethanol. Connect the flask to the reflux condenser and boil gently until the soap has completely dissolved. Cool to about 70°C. Titrate with the ethanolic solution of hydrochloric acid until the colour is just perceptibly pink, identical with that obtained when the ethanol was neutralised.

6.1.3 **Calculation.** Free caustic alkali per cent by weight, expressed as $Na_2O = \frac{0.31V}{W}$

where W = the weight in grammes of the test portion
and V = the volume in millilitres of 0.1N ethanolic hydrochloric acid solution used.

6.2 Method 2

Method 2 (barium chloride method) should be applied to all soft potassium soaps or mixed sodium and potassium soaps.

6.2.1 **Reagents.**

(i) Ethanol, 95 per cent (v/v).
(ii) Barium chloride, 10 per cent solution.
(iii) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.
(iv) Hydrochloric acid, 0.1 N solution.

6.2.2 **Procedure.** Dissolve 10g of the sample in 100 ml of the ethanol rendered neutral and containing 0·8 ml of phenolphthalein indicator. Add, in a thin stream, 5 ml of the barium chloride solution, previously heated and neutralized. Mix thoroughly and titrate with hydrochloric acid at 70°C, until the pink colour disappears.

6.2.3 **Calculation.** Free caustic alkali, per cent by weight, expressed as $Na_2O = \frac{0.31\ V}{W}$

where W = weight, in grammes, of test portion taken
and V = volume, in millilitres, of 0.1 N hydrochloric acid required.

7. DETERMINATION OF TITRE OF FATTY ACIDS OR TOTAL FATTY MATTER

7.1 **Definition.** The titre of an oil or fat is the highest temperature reached when the liberated water-insoluble fatty acids are crystallizing under arbitrarily controlled conditions.

The titre is generally taken to represent the solidification point of the fatty acids, although they actually solidify over a range of temperature.

7.2 **Principle.** An aqueous solution of the soap is decomposed with sulphuric acid and the liberated water-insoluble fatty acids are separated, washed free from mineral acid and dried. Titre is then determined on these fatty acids.

7.3 **Reagents.**

(i) Sulphuric acid, approximately 30 per cent (w/v).
Add 1 volume of sulphuric acid, [d=1.84 to 4 volumes of water.]

(ii) Methyl orange indicator, 0.04 per cent (w/v) aqueous solution.

7.4 **Apparatus.** The assembly of the apparatus is shown in Fig. 1 and the details of the constituent parts are as follows:

(i) Titre tube, of glass, provided at the top with a rim or flange and having the following dimensions:

External diameter	31.0 — 32.0 mm
Length	90 — 100 mm
Wall thickness	2.0 — 3.0 mm

The tube carries a mark at 57 mm from the bottom to show the height to which the tube is subsequently to be filled and is inserted in a cork so that it may be held centrally in the wide-mouthed bottle (ii).

(ii) Wide-mouthed bottle, of glass, conforming to the following dimensions:

Diameter	60 — 100 mm
Capacity	400 — 800 ml

The bottle shall be loaded with just sufficient lead shot to make it sink and be reasonably stable when it is immersed in the water-bath.

(iii) Water-bath, any suitable bath complying with the following requirements:

Water level: 10 mm above the 57 mm mark on the titre tube.
Temperature of water surrounding the bottle: $20 \pm 1°C$ for all samples having titres 35°C or higher; 15-20°C below the titre point for all other samples.

(iv) Thermometers (a) Range 0-60°C in 0.1°C steps, calibrated for 45 mm immersion for reading the titre.
(*b*) a general purpose thermometer of suitable range.

(v) Stirrer, of glass, stainless steel, or suitable alloy, rod of 2-3mm diameter. One end shall be bent in the form of a loop, of 19 mm outside diameter, at right angles to the shaft of the stirrer. The stirrer is used to agitate the fatty acids immediately before reading the titre.

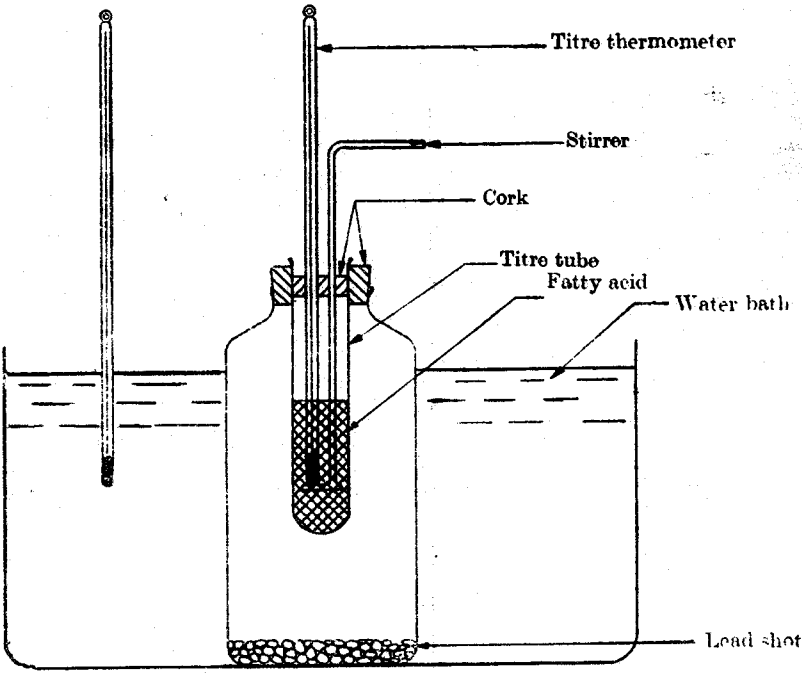

Fig. 1. Apparatus for the determination of titre.

7.5 **Procedure for preparing fatty acids.** Dissolve 40-50g of the sample in 400ml of hot water in a 600ml beaker. When solution is complete, add gradually with stirring an excess of dilute sulphuric or hydrochloric acid. Heat the beaker and stir the contents until the liberated fatty acids form a clear layer on the top.

Siphon or draw off the water underneath as completely as possible, wash the fatty acids first with 500 ml of hot distilled water, which is drawn off, and then with another 500 ml of hot water which is also drawn off as completely as possible. Alternatively, cooling and stirring to solidify, and reheating may produce a quicker separation. Filter the fatty acids through a dry paper containing a small amount of anhydrous sodium sulphate until free from moisture and allow the fatty acids to solidify.

These fatty acids are now ready for determination of the titre.

7.6 **Procedure for determining titre.** Fill a titre tube to the 57 mm mark with the fatty acids: when these have cooled to about 15°C above the expected titre, place the tube in the assembly with the flanged rim close to the top of the cork. Insert the titre thermometer to the appropriate immersion mark, the thermometer being supported centrally by a cork, through which also passes the stirrer.

Before the temperature of the fatty acids drops to a value 10°C above the expected titre, commence agitation in a vertical manner at a rate of 100 complete up-and-down motions per minute, the stirrer moving through a vertical distance of about 38 mm. Continue stirring in this manner until the temperature has remained constant for 30 seconds, or has begun to rise within 30 seconds of ceasing to fall. Discontinue stirring immediately and lift the stirrer out of the sample.

Observe the rise in temperature: the highest temperature reached after the stirring ceases is the titre.

When making the titre reading, avoid all undue vibration as this will cause the temperature to drop before reaching the maximum.

8. DETERMINATION OF UNSAPONIFIED MATTER

Unsaponified matter comprises:

(*a*) free fatty acids
(*b*) unsaponified neutral fat and
(*c*) unsaponifiable matter.

8.1 Determination of free fatty acids (*a*)

8.1.1 Reagents.

(i) Ethanol, 95 per cent (v/v).
(ii) Potassium hydroxide, 0.1N ethanolic solution.
(iii) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.

8.1.2 **Procedure.** Add 0.5 ml of the phenolphthalein solution to 100 ml of boiling ethanol in a suitable beaker, allow to cool to 70°C and neutralize at this temperature with the ethanolic potassium hydroxide solution. Dissolve in this solution 5g of the soap as quickly as possible by heating. If the solution is not alkaline, titrate with the ethanolic potassium hydroxide solution until the faint pink colour persists for 15 seconds, maintaining the temperature at 70°C throughout the titration.

8.1.3 **Calculation.** Free fatty acids, per cent by weight.

(*a*) expressed as oleic acid $= \frac{2.82 \times V}{W}$

(*b*) expressed as lauric acid $= \frac{2.00 \times V}{W}$

where V = volume, in millilitres, of 0.1 N ethanolic potassium hydroxide required

and W = weight, in grammes, of the test portion taken.

8.2 **Determination of unsaponified neutral fat and unsaponifiable matter** (b and c)

8.2.1 **Reagents.**

(i) Ethanol, 95 per cent (v/v).
(ii) Diethyl ether.
(iii) Potassium hydroxide, 0.5N aqueous solution.
(iv) Phenolphthalein indicator, 0.5 per cent solution (w/v) in 95 per cent (v/v) ethanol.
(v) Acetone
(vi) Potassium hydroxide, 0.5N ethanolic solution.

8.2.2 **Procedure.** Dissolve 5g of the soap in about 80 ml of a mixture of 50 ml of ethanol, and 100 ml of water, with heating if necessary; transfer to a separating funnel, washing the beaker with the remaining 70 ml of the dilute ethanol. Extract with 100 ml of the diethyl ether while still slightly warm, run off the ethanolic soap layer into a second separating funnel and repeat the extraction with 50 ml of the ether. Extract the lower layer again with a further 50 ml of the ether, and pour the three ethereal extracts into a separating funnel containing 20 ml of water. Rotate the separating funnel gently without violent shaking and after allowing to separate, run off the wash water. Repeat the washing with water in the same way until the separated water is not more than faintly turbid when acidified. Wash the ethereal solution twice by shaking vigorously with 20 ml of the aqueous potassium hydroxide solution, each washing with alkali being immediately followed by washing with 20 ml of water, shaking vigorously each time.

Acidify the last alkaline washing after separating it and, if the liquid becomes turbid, repeat the washings with the aqueous potassium hydroxide and water until the final alkali washing remains clear on acidification. Finally wash

with successive quantities of 20 ml of water until the water no longer gives a pink colour with phenolphthalein. Transfer the ethereal solution to a weighed flask, evaporate the ether and add 2-3 ml of acetone. With the aid of a gentle current of air, remove the solvent completely from the flask, which is preferably almost entirely immersed, held obliquely, and rotated in boiling water. Repeat the last operation until the weight of the residue is constant. The residue consists of unsaponified neutral fat and unsaponifiable matter.

After weighing, dissolve the contents of the flask in 10 ml of freshly boiled and neutralized ethanol and titrate with 0.1N ethanolic potassium hydroxide solution to phenolphthalein—not more than 0.1 ml should be required for neutralization. If more is required, the test has not been effectively carried out and must be repeated.

8.3 Determination of unsaponifiable matter

8.3.1 Reagents.

(i) Potassium hydroxide, 0.5N ethanolic solution.

8.3.2 Procedure. Evaporate the solution remaining from the titration given under the "Determination of unsaponified neutral fat and unsaponifiable matter" until the bulk of the ethanol is removed. Add 25 ml of the ethanolic potassium hydroxide solution and boil under a reflux condenser for half an hour. Transfer the ethanolic soap solution to a separating funnel with the aid of 50 ml of water, and repeat the process of ether extraction, washing etc. described above. Weigh the final residue of unsaponifiable matter.

8.3.3 Calculation. Unsaponifiable matter, per cent by weight

$$= \frac{W_2 \times 100}{W}$$

Unsaponified neutral fat, per cent by weight

$$= \frac{100(W_1 - W_2)}{W}$$

where W = weight in grammes of test portion taken orginally.

W_1 = weight in grammes of residue from the unsaponified neutral fat and unsaponifiable matter method

and W_2 = weight in grammes of residue after saponification.

Total free fat or unsaponified saponifiable matter, per cent, by weight = B + C

where B = percentage of free fatty acids
and C = percentage of unsaponified neutral fat.

9. DETERMINATION OF MATTER INSOLUBLE IN ETHANOL

9.1 Reagents.

(i) Ethanol, 95 per cent (v/v).

(ii) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.

9.2 Procedure. Dry 5g of soap in a tared beaker by adding 10 ml of the ethanol and evaporating to dryness on a steam bath. Repeat this process three times and finally dry the soap to constant weight at 100°C. Dissolve the dried soap in 100 ml of the ethanol, previously made neutral to phenolphthalein. Filter the solution through a previously dried (at 100°C) and weighed filter paper or through a weighed Gooch or sintered glass crucible with suction. (The solution should be protected from carbon dioxide and other acid fumes during the operation.) Transfer the insoluble matter completely to the filter paper and wash thoroughly with hot neutral ethanol, until all the soap has been removed. Dry the paper with its contents at 100°C and then weigh. Weighing of paper should be done in a stoppered weighing bottle.

9.3 Calculation. Matter insoluble in ethanol, per cent by weight

$$= \frac{100 W_1}{W}$$

where W = weight in grammes, of test portion taken
and W_1 = weight, in grammes, of residue after drying.

10. DETERMINATION OF MATTER INSOLUBLE IN WATER

10.1 Reagents.

(i) Ethanol, 95 per cent (v/v).

(ii) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.

10.2 Procedure. Dry 5g of soap in a tared beaker by adding 10 ml of alcohol and evaporating to dryness on a steam-bath. Repeat this process three times and finally dry the soap to constant weight at 100°C. Dissolve the dried soap in 100 ml of the ethanol, previously made neutral to phenolphthalein. Filter the solution through a previously dried (at 100°C) and weighed filter paper or through a weighed Gooch or sintered glass crucible with suction. (The solution should be protected from carbon dioxide and other acid fumes during the operation). Transfer the insoluble matter to the filter paper and wash thoroughly with hot neutral ethanol, until all the soap has been removed. Change the receivers, extract the residue with water at 60°C and wash the filter thoroughly. Dry the filter and residue at 100°-105°C for 3 hours, and weigh the matter insoluble in water.

11. DETERMINATION OF CHLORIDES

11.1 Reagents.

(i) Nitric acid, d=1.3 to 1.4.

(ii) Silver nitrate, 0.1N aqueous solution.

(iii) Ammonium thiocyanate, 0.1N aqueous solution.

(iv) Ammonium ferric sulphate, 10 per cent (w/v) aqueous solution.

11.2 Procedure. Weigh approximately 5g of soap into an evaporating basin, to an accuracy of 0.01g and dissolve in 50 ml of distilled water. Transfer the solution quantitatively to a 200 ml graduated flask. Wash with small portions of distilled water. Add 5ml of the nitric acid and then immediately add exactly 25 ml of silver nitrate solution, using a pipette. Place on a water-bath until the fatty acids are completely separated and the silver chloride formed has collected in a mass.

Cool to room temperature and dilute to the mark with distilled water. Mix by shaking and filter through a dry, pleated filter paper. Discard the first 10 ml and then collect 100 ml of filtrate. Add 2-3 ml of the ammonium ferric sulphate solution and titrate with the ammonium thiocyanate solution.

11.3 Calculation. Chlorides, per cent by weight:

(i) as sodium chloride (NaCl)

$$= 0.0585\ (25\times 0.1-2\times 0.1\times V)\times\frac{100}{W}$$

(ii) as potassium chloride (KCl)

$$= 0.0746\ (25\times 0.1-2\times 0.1\times V)\times\frac{100}{W}$$

where W = weight in grammes of test portion taken
and V = volume in millilitres of 0.1N ammonium thiocyanate solution required.

12. DETERMINATION OF PHENOLS

12.1 Principle. The soap is precipitated with calcium or magnesium nitrate and the phenolic substances separated by filtration. The bromo-derivatives are formed by the addition of a known amount of standard bromide-bromate solution; the excess of bromine is determined by the addition of potassium iodide and titration of the liberated iodine with standard thiosulphate solution.

Phenol and m-cresol each form tri-bromo derivatives whereas o-cresol and p-cresol form only dibromo derivatives. Therefore one of the three phenolic standard solutions listed below shall be used.

12.2 Reagents.

(i) Hydrochloric acid solution, containing 20 per cent (w/w) of HCl (d = 1.10).

(ii) Sodium hydroxide, N solution.

(iii) Sodium hydroxide, 10 per cent (w/v) solution.

(iv) Calcium nitrate or magnesium nitrate, 20 per cent (w/v) solution.

(v) Potassium iodide, 10 per cent (w/v) solution.

(vi) Bromide-bromate solution. Dissolve 19.8g of potassium bromide and 5.6g of potassium bromate in water and dilute to 1000 ml.

(vii) Sodium thiosulphate, 0.2N solution.

(viii) Standard phenolic solution. Dissolve 1.0g of the standard substance, selected from one of the following, in 10 ml of N sodium hydroxide solution and dilute to 1000 ml.

(*a*) Phenol or

(*b*) Cresols consisting of a mixture of 35, 40 and 25 per cent of o-cresol, m-cresol, and p-cresol, respectively or

(c) A sample of the particular phenolic substances used in the preparation of the soap under examination.

(ix) Soap, free from phenols, and containing approximately 60 per cent of total fatty matter.

(x) Starch indicator solution.

12.3 Procedure. Weigh 5g of the sample into a 250 ml squat beaker and add 10 ml of the sodium hydroxide solution. Half fill the beaker with water and heat on a steam-bath until the soap is dissolved. Transfer to a 1000 ml volumetric flask, dilute to about 700 ml, add 25 ml of the calcium nitrate or magnesium nitrate solution, cool, adjust to 1000 ml and mix thoroughly. Filter slightly more than 100 ml and measure out 100 ml into a 1 litre stoppered bottle. Add 100 ml of water, 50 ml of the bromide-bromate solution and 10 ml of the hydrochloric acid solution.

Allow to stand for 60 minutes, then add 25 ml of the potassium iodide solution, insert the stopper and mix thoroughly. Titrate the liberated iodine with the standard sodium thiosulphate solution, using the starch solution as indicator.

Test on blank and standard.

Following the same procedure as for the sample above, carry out a test on a blank and standard prepared as follows:

(i) Blank, prepared from 5g of the soap, free from phenols, omitting the sample.

(ii) Standard, prepared from 5g of the soap, free from phenols, to which 25 ml of the appropriate standard phenolic solution has been added, omitting the sample.

12.4 Calculation. Phenolic substances, per cent by weight:

$$= \frac{5 \times V_1 - V_3}{V_1 - V_2}$$

where V_1 = volume in millilitres of 0.2N sodium thiosulphate solution required for the blank,

V_2 = volume in millilitres of 0.2N sodium thiosulphate solution required for the standard

and V_3 = volume in millilitres of 0.2N sodium thiosulphate solution required for the sample.

13. DETERMINATION OF TOTAL SILICA

13.1 Method 1. Gravimetric.

13.1.1 **Principle.** The material is ignited, the ash fused, dissolved in mineral acid and the solution evaporated to dryness to convert silicic acid to silica. Silica is separated by filtration and weighed.

13.1.2 **Reagents.**

(i) Hydrochloric acid, concentrated, d=1.18

(ii) Sulphuric acid, concentrated, d=1.84

(iii) Hydrofluoric acid, 48 per cent (w/w) solution.

(iv) Fusion mixture. Mix equal parts of anhydrous sodium carbonate and sodium nitrate.

13.1.3 **Procedure.** Weigh, to the nearest milligramme, about 3g of the soap into a platinum dish, add 5g of the sodium carbonate/sodium nitrate mixture, mix and ignite carefully to destroy all organic matter and resulting carbon and then fuse. Cool the mass and dissolve it in hot water. Transfer the solution completely to a porcelain basin, cover with a clock-glass and acidify with the hydrochloric acid. Evaporate to dryness on a steam bath.* add 5 ml of the hydrochloric acid to the residue and again evaporate to dryness. Bake for 30 minutes at 130°C to dehydrate the silicic acid, cool, add 5 ml of the hydrochloric acid solution and sufficient hot water to effect solution of soluble electrolytes, and filter through a hardened filter paper.† Transfer the insoluble matter completely to the filter paper with hot water and wash the filter paper with hot water until the wash liquor is free from chlorides. Ignite in a platinum crucible previously ignited to constant weight, cool in a desiccator and weigh as SiO_2.

Add 10 ml of the hydrofluoric acid solution and 4 drops of the sulphuric acid to the crucible and evaporate to dryness over a low flame. Ignite and reweigh as before.

* If borates are present, modify the method as follows: Moisten the residue with a little hydrochloric acid, add 25 ml of anhydrous methanol and evaporate to dryness. Repeat this step six times, and continue if necessary until all boric acid has been removed as methyl borate.

† A Whatman No. 541 filter paper is suitable.

13.1.4 Calculation. Total silica, per cent by weight

$$= \frac{100\ (W_1 - W_2)}{W}$$

where W_1 = weight in grammes of residue,
W = weight in grammes of sample taken
and W_2 = weight in grammes of residue after treatment with hydrofluoric acid.

13.2 Method 2. Colorimetric

13.2.1 Principle. All organic matter is burnt away at a low temperature, the ash is fused and the melt dissolved in water. Ammonium molybdate is added to the acidified solution, whereby soluble yellow silicomolybdic acid is formed. The optical density, which is proportional to the silica concentration, is measured at a wave-length of 420mμ.

Interference due to phosphates is avoided by adding citric acid, which decomposes the analogous phosphomolybdic acid but has, under the test conditions, no effect on the silicomolybdic acid.

13.2.2 Reagents.

(i) Sulphuric acid, 1 per cent (v/v) solution. Add 10 ml of sulphuric acid, d=1.84, cautiously with stirring to 1000 ml of water and cool.

(ii) Ammonium molybdate, 10 per cent (w/v) solution.

(iii) Citric acid, 25 per cent (w/v) solution

(iv) Fusion mixture. Thoroughly mix 14 g of potassium carbonate with 11 g of anhydrous sodium carbonate in a mortar.

(v) Standard silica solution. Fuse 0.2 g of pure silica, which has been ignited just prior to weighing, with 2g of the fusion mixture in a platinum crucible until effervescence ceases and a clear melt is obtained. Cool and dissolve the melt in the crucible in hot water. Cool, transfer the solution quantitatively to a 1000 ml volumetric flask and dilute to the mark with freshly boiled and cooled water. Store the solution in a clean, dry, polythene, wax-coated glass or hard, rubber bottle (1 ml contains 0.2 mg SiO_2). This solution is stable.

The reagents should yield a low blank value and it is, therefore, essential that they should be as free as possible from traces of silica.

13.2.3 **Procedure.** Weigh to the nearest milligramme, into a platinum crucible, a quantity of soap powder which contains 20-30 mg of SiO_2 and add 0.5g of the fusion mixture. Burn off the soap at as low a temperature as possible. continue heating until the ash is completely fused, cool and dissolve the melt in hot water. Cool the solution, transfer quantitatively to a 500 ml volumetric flask, and dilute to the mark.

Note. Carry out the colorimetric determination as soon as possible after preparation of the test solution, as the latter slowly dissolves silica from the glass. thus yielding high results.

Pipette a 20 or 25 ml portion of the solution of the ash into a 100 ml volumetric flask, add 20 ml of the sulphuric acid solution and dilute to about 50 ml with water. Add from a pipette 5 ml of the ammonium molybdate solution, mix well and allow to stand for 10 minutes for full colour development to occur. Add from a pipette 2 ml of the citric acid solution, adjust the volume to 100 ml and mix well.

Immediately measure the optical density of the solution at 420 mμ in a 1 cm all-glass cell in the spectrophotometer, against a blank containing all the reagents but no silica. Read off the silica content from a calibration curve.

13.2.4 **Preparation of calibration curve.** Measure into separate 100 ml volumetric flasks, by means of a graduated pipette or microburette, volumes of the standard silica solution containing 0.5, 0.75, 1.0 and 1.5 mg of silica (SiO_2). Add 20 ml of the sulphuric acid solution and dilute each solution to about 50 ml with water.

To each flask add 5 ml of the ammonium molybdate solution, mix well and allow to stand for 10 minutes. Add 2 ml of the citric acid solution, adjust the volume to 100 ml and again mix well.

Immediately measure the optical density of the solutions at 420 mμ in a 1 cm all-glass cell in the spectrophotometer, against a blank prepared in a similar manner but containing no silica.

Construct a curve by plotting optical densities against milligrammes of silica. It is necessary to construct a new graph when a fresh set of reagents is brought into use.

13.2.5 **Calculation.** Total silica, SiO_2, per cent by weight

$$= \frac{50W_1}{VW}$$

where W_1 = weight in milligrammes of silica read from calibration curve.

W = weight in grammes of test portion taken

and V = volume, in millilitres, of solution of ash taken.

14. DETERMINATION OF TOTAL PHOSPHATE

Two alternative methods are given, a gravimetric method and a potentiometric titration method.

14.1 Method 1. Gravimetric

14.1.1 **Principle.** The total phosphate content is determined gravimetrically as magnesium pyrophosphate. If borate and heavy metals are absent and silicate is present, the sample is ignited to destroy organic matter, the residue dissolved in dilute hydrochloric acid and the solution evaporated to dryness to convert silicic acid into silica. The silica is removed and complex phosphates converted into the orthomodification by boiling with dilute hydrochloric acid. The phosphate is precipitated as magnesium ammonium phosphate, ignited and weighed as magnesium pyrophosphate. When heavy metals, silicates and borates are present the product is ignited in the same manner to destroy organic matter.

The residue is dissolved in dilute hydrochloric acid, and the solution is evaporated to dryness to convert silicic acid into silica. The silica and boric acid are removed, and the solution is heated with nitric acid to destroy chlorides. The phosphate is then precipitated as phosphomolybdate, the precipitate isolated by filtration, and washed in dilute nitric acid to remove any heavy metals. It is then dissolved in ammonia and the phosphate finally precipitated as magnesium ammonium phosphate.

14.1.2 When silicate is the only interfering radical:

14.1.2.1 Reagents.

(i) Hydrochloric acid. d=1.18

(ii) Magnesia mixture. Dissolve 55g of crystalline magnesium chloride and 105g of ammonium chloride in water, and 1 ml of the hydrochloric acid and dilute to 1000 ml.

(iii) Fusion Mixture. Mix equal parts of anhydrous sodium carbonate and sodium nitrate.

(iv) Glacial acetic acid.

(v) Aqueous ammonia, d=0.880.

(vi) Aqueous ammonia, 2 per cent (v/v).

14.1.2.2 Procedure. Weigh to the nearest milligramme, into a platinum dish, sufficient of the product to yield about 1 g of magnesium pyrophosphate, add about twice its weight of the fusion mixture, mix thoroughly and heat gently over a low bunsen flame to destroy all organic matter. Dissolve the residue in water and transfer the solution to an evaporating basin, acidify with the hydrochloric acid and evaporate to dryness to convert silicic acid to silica. Moisten the residue with a little hydrochloric acid and again evaporate to dryness. Moisten the residue with a little hydrochloric acid, dissolve in water, filter the solution through a hardened filter paper* into the beaker and wash the basin thoroughly with water, passing each wash in turn through the filter paper, and finally wash the paper thoroughly with water. Add 10 ml of the hydrochloric acid to the filtrate, boil gently for 15 minutes to ensure that all phosphate is present in the ortho-form. Add 5 ml of glacial acetic acid, 50 ml of the magnesia mixture and add aqueous ammonia d=0.880, dropwise until the solution is alkaline to phenolphthalein and then add a further 50 ml of the aqueous ammonia d=0.880.

* A Whatman No. 541 is suitable.

Allow the precipitate to stand overnight, transfer the supernatant liquor through a tared Gooch crucible packed with acidwashed asbestos, wash the precipitate with 100 ml of the 2 per cent aqueous ammonia, transfer the precipitate completely to the Gooch filter crucible and wash thoroughly with the 2 per cent aqueous ammonia until the washings are free from chlorides. Dry the crucible, ignite gently at first and then heat strongly until a red glow has spread completely over the whole precipitate; when this occurs the phosphate has been converted quantitatively to magnesium pyrophosphate. Cool the crucible in a desiccator and weigh.

14.1.3 When silicate, borate and heavy metals are present:

14.1.3.1 Reagents.

(i) Methanol, anhydrous.

(ii) Hydrochloric acid, d=1.18

(iii) Nitric acid, d=1.42

(iv) Molybdate reagent. Dissolve 90 g of ammonium molybdate in hot water, add 240 g of ammonium nitrate and when this has dissolved, cool the solution, add 100 ml of 6N aqueous ammonia and dilute to 1000 ml.

(v) Nitric acid, 1 per cent (v/v) solution.

(vi) Fusion mixture. Mix equal parts of anhydrous sodium carbonate and sodium nitrate.

14.1.3.2 Procedure. Weigh to the nearest milligramme, into a platinum dish, sufficient of the soap to yield about 1 g of magnesium pyrophosphate, add about twice its weight of the fusion mixture, mix thoroughly and heat gently over a small bunsen flame to destroy all organic matter. Dissolve in water and transfer the solution to an evaporating basin, acidify with the hydrochloric acid and evaporate to dryness to convert silicic acid to silica. Moisten the residue with a little water, add 5 ml of the hydrochloric acid and again evaporate to dryness. Cover the basin with a clock-glass, moisten with a little hydrochloric acid, add 50 ml of the methanol and evaporate to dryness. Repeat this step at least a further six times or until all boric acid has been removed.

Rinse the clock-glass with water, collecting the rinsings in the basin, add 20 ml of the nitric acid, d=1.42, and evaporate to dryness; repeat this treatment with 10 ml of nitric acid to ensure that all chloride has been destroyed. Moisten the residue with a little nitric acid, dissolve in distilled water and filter the solution through a hardened filter paper† into a beaker. Wash the contents of the basin completely into the filter paper and wash the paper thoroughly with water. To the filtrate add 10 ml of the nitric acid, d=1.42, raise to the boil and boil gently for thirty minutes. Cool the solution to 70°C add 150 ml of molybdate reagent also at 70°C and maintain at 70°C for fifteen minutes. Filter through a further hardened filter paper† and wash the precipitate thoroughly with cold (0–4°C) 1 per cent nitric acid solution to ensure that heavy metals are completely removed. Dissolve the precipitate in ammonium hydroxide and precipitate and determine as described previously.

14.1.3.3 **Calculation.** Total phosphate expressed as phosphoric oxide, P_2O_5, per cent by weight

$$= \frac{63.8W_1}{W_2}$$

where W_1 = weight of magnesium pyrophosphate

and W_2 = weight of sample taken.

14.2 Method 2. Potentiometric titration

14.2.1 **Principle.** Organic matter is destroyed by ashing and the inorganic matter is extracted from the ash with water. The aqueous solution is made acid and boiled, in order to hydrolyse any condensed phosphates present into the orthophosphate. The solution is filtered and a convenient aliquot portion taken. The pH is adjusted to 4.5 to convert the ortho-phosphate into the sodium dihydrogen salt (NaH_2PO_4) and silver nitrate solution is added. Nitric acid is liberated in stoichiometric equivalence to the phosphate originally present, and this acid is determined by titration with 0.2N sodium hydroxide solution.

†A Whatman No. 542 is suitable.

The essential reaction is:
$NaH_2PO_4 + 3\,AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3$
Silicate and borate do not interfere.

14.2.2 Reagents.

(i) Sodium nitrate ($NaNO_3$).

(ii) Nitric acid, 50 per cent (v/v) solution.

(iii) Silver nitrate, 15 per cent (w/v) solution, kept in a brown bottle.

(iv) Sodium hydroxide, 6 per cent (w/v) solution.

(v) Sodium hydroxide, 0.2N solution, accurately standardized.

(vi) Indicator. An indicator which will indicate a pH of 4.5 is required.

Alternatively, a pH meter can be used.

14.2.3 Apparatus. Potentiometric titration apparatus, comprising:

(i) Glass electrode.

(ii) Silver electrode.

(iii) Millivoltmeter. An instrument suitable for observing the change in potential of a solution using glass and silver electrodes. Most pH meters designed for use with glass electrodes are suitable.

14.2.4 Procedure. Remove organic matter by charring before employing the general procedure. This is best done in the case of powders by transferring a known weight (containing of the order of 0.7 g P_2O_5) to a flat 10 cm silica dish, adding a few grammes of the sodium nitrate and placing in a muffle furnace at 660°C for 30 minutes. Extract the cooled charred mass with hot water into a 250 ml squat beaker, then adjust the total volume of liquor to about 150 ml.

Add 10 ml of the nitric acid solution to hydrolyse the phosphates, insert some boiling aid (such as porcelain chips), then boil for 45 minutes, keeping a cover glass over the beaker. An electric hotplate is convenient for this operation. Cool and dilute to 250 ml.* Filter a portion into a suitable vessel.

*A Whatman No. 541 is suitable.

Pipette a convenient portion of the filtrate into a 250 ml beaker, add a further quantity of water and finally a few drops of the indicator. Adjust to pH 4.5 by using first the 6 per cent sodium hydroxide solution, followed by the 0.2N sodium hydroxide solution, to give an end point at pH 4.5.

Connect the millivoltmeter to the glass electrode (negative) and the silver electrode (positive) and insert both electrodes into the test solution. Add 10 ml of the silver nitrate solution, stir thoroughly and take a millivoltmeter reading. Add successive quantities of the 0.2N sodium hydroxide solution, stirring continuously, until the millivoltmeter reading has risen by about 70 mV. Thereafter add the titrant in 0.2 ml amounts until the potential difference changes by 5 mV/0.2 ml. Note or plot on graph paper the millivoltmeter reading after every addition. Continue the titration through the end point by adding only 0.1 ml at a time until the point of inflexion of the potential difference ml NaOH curve has been well passed. The point of inflexion can then be determined either from the readings or by noting the point of maximum change of potential difference with the increments of sodium hydroxide solution. Read the volume of titrant used (T ml) at the inflexion point.

14.2.5 **Calculation.** Total phosphates expressed as phosphoric acid P_2O_5, per cent, by weight

$$= \frac{0.7093V}{W} \times \frac{250}{V_1}$$

where V_1 = volume in millilitres, of 0.2N sodium hydroxide solution used,

W = weight, in grammes, of test portion taken

and V_2 = volume, in millilitres, of test solution taken for titration.

15. DETERMINATION OF ROSIN

15.1 Method 1. Qualitative test

15.1.1 **Reagents.**

(i) acetic anhydride

(ii) Sulphuric acid, sp. gr. 1.53.

15.1.2 **Procedure.** Dissolve 40-50 g of the soap in 400 ml of hot water in a suitable beaker and to this solution add gradually an excess of dilute sulphuric acid or hydrochloric acid.

Heat the beaker and draw off the water underneath the liberated fatty acids which would have formed a clear layer on the top. Wash the fatty acids twice with 500 ml portions of boiling water. Filter the fatty acid through dry paper. Boil a few drops of the fatty acids with 2-3 ml of acetic anhydride in a dish, allow to cool and add sulphuric acid drop by drop. If rosin is present, the characteristic violet colour is produced which changes to brown.

15.2 Method 2. Quantitative determination

15.2.1 Reagents.

(i) Naphthalene—2-sulphonic acid solution. Dissolve 40g of naphthalene—2-sulphonic acid in 1000 ml of pure dry methanol.

(ii) Sulphuric acid, dilute solution.

(iii) Potassium hydroxide. 0.2N ethanolic solution. Standardize against standard sulphuric or hydrochloric acid solution each time the solution is used.

(iv) Phenolphthalein indicator, 0.5 per cent (w/v) solution in 95 per cent (v/v) ethanol.

15.2.2 Procedure. Separate the total fatty matter from about 5g of the soap by dissolving in hot water, acidifying with dilute sulphuric acid, cooling and washing the cake of fatty matter with water until the aqueous washings are free from acidity. The fatty matter may also be obtained by extraction with diethyl ether. Weigh about 2g of the total fatty matter into a 150 ml flask, dissolve it in 20 ml of the naphthalene—2-sulphonic acid solution and boil gently under a reflux condenser for 30 minutes, adding small pieces of pot to ensure regular ebullition. Carry out a blank test at the same time with 20 ml of the naphthalene-2-sulphonic acid solution alone. Cool the contents of both flasks and titrate with the potassium hydroxide solution, using 0.5 ml of the phenolphthalein indicator.

15.2.3 **Calculation.** Rosin acids, per cent, by weight of total fatty matter

$$= \frac{6.52\ (V\text{-}V_1) - 1}{W}$$

and rosin, per cent, by weight of total fatty matter

$$= \frac{6.9\ (V\text{-}V_1) - 1}{W}$$

where V = volume, in millilitres, of 0.2N potassium hydroxide solution required by the sample,

V_1 = volume in millilitres, of 0.2N potassium hydroxide solution required by the blank

and W = weight, in grammes, of total fatty matter taken.

16. DETERMINATION OF GLYCEROL

Two methods are given. The first employs periodic acid as oxidising agent, and the periodic acid consumed, which is determined iodimetrically, is a measure of the glycerol oxidised. The second uses sodium metaperiodate and the glycerol content of the sample is assessed from the formic acid produced during its oxidation. The latter method gives a direct measure of glycerol present and provided that no sugars are present, is specific for glycerol. It is to be preferred, therefore, for arbitration purposes, as the iodimetric method is not specific for glycerol even though it is more sensitive.

It is essential that the reaction shall take place in the dark.

16.1 Method 1. Using periodic acid

16.1.1 **Reagents.**

(i) Chloroform. Check by running a blank test on the periodic acid solution, with and without 50 ml of chloroform. The difference should not exceed 0.5 ml.

(ii) Acetic acid, glacial.

(iii) Hydrochloric acid, d=1.18.

(iv) Periodic acid solution. Dissolve 5.4g of periodic acid in 100 ml water and add 1900 ml of glacial acetic acid. Mix thoroughly. Store in a stoppered glass bottle in the dark.

(v) Potassium iodide, 15 per cent (w/v) solution.

(vi) Potassium dichromate, 0.1 N solution.

(vii) Sodium thiosulphate, 0.1 N solution.

(viii) Starch indicator solution. Prepare by making a paste of 10 g of soluble starch in water. Add to this 1 litre of boiling water, stir rapidly and cool. 1.25g of salicylic acid may be added as a preservative. Store at 4-10°C. Test before use by placing 2 ml in 100 ml of water and adding 0.05 ml of 0.1N iodine solution. The deep blue colour should be discharged by 0.05 ml of the thiosulphate solution.

16.1.2 Standardization of sodium thiosulphate solution. Pipette 25 ml of the potassium dichromate solution into a beaker. Add 5 ml of the hydrochloric acid, 10 ml of the potassium iodide solution and rotate to mix. Allow to stand for 5 minutes and then add 100 ml of water. Titrate with the sodium thiosulphate solution, stirring continuously, until the yellow colour has almost disappeared. Add 1-2 ml of starch indicator solution and continue the titration adding the sodium thiosulphate solution slowly until the blue colour has just disappeared.

Normality of sodium thiosulphate solution

$$= \frac{2.5}{V}$$

where V = volume, in millilitres, of sodium thiosulphate solution required.

16.1.3 Procedure. Weigh, to the nearest milligramme, approximately 10g of the sample. Add 91 ml of chloroform, measured from a burette to within ± 0.2 ml to a 1000 ml volumetric flask. Add 25 ml of the glacial acetic acid.

Transfer the sample to the flask and add approximately 500 ml of water. Stopper and shake until the sample is dissolved, warming if necessary and cooling before proceeding further. Dilute to the mark with water, stopper and mix. Allow to stand until the layers have separated.

Pipette 50 ml of periodic acid solution into a series of 400 ml beakers. Prepare two blanks by adding 100 ml of water to each. Pipette 100 ml of the aqueous solution into one of the beakers containing 50 ml of the periodic acid solution, shake gently to effect thorough mixing. Cover with a watch glass and allow to stand for 30 minutes in the dark.

Add 20 ml of the potassium iodide solution, mix by shaking gently, and allow to stand for at least 1 minute, but never for more than 5 minutes before titrating. Do not allow to stand in bright or direct sunlight. Dilute to approximately 200 ml with water and titrate with the sodium thiosulphate solution. Use a variable-speed electric stirrer to keep the solution thoroughly mixed. Continue the titration to the disappearance of the brown iodine colour. Add 2 ml of starch indicator solution and continue the titration, to the disappearance of blue iodo-starch colour. Read the burette to 0.01 ml. Treat the blanks in the same way.

If the volume of titrant required by the sample is less than 0.8 of the volume required by the blank, repeat the test using a smaller portion of the sample solution. If 10 ml or less of the sample solution only is required repeat using a smaller sample (less than 2g) in preparing the solution.

Note 1. If the aqueous solution contains suspended matter, filter before pipetting the portions for test.

Note 2. Solutions of samples should not be allowed to stand in bright or direct sunlight or for more than $1\frac{1}{2}$ hours at room temperature.

Note 3. If the sample contains more than 10 per cent of moisture, adjust the amount of chloroform added so that the total volume of fatty acid and chloroform is 100 ± 1 ml.

Note 4. If the aqueous phase is alkaline because of large amounts of builders in the sample, add sulphuric acid, d=1.84 in 0.5 ml increments until the solution is acid to litmus.

16.1.4 **Calculation.** Free glycerol, per cent, by weight

$$= \frac{2.302N\,(V-V_1)}{W}$$

where N = normality of the sodium thiosulphate solution

V = volume, in millilitres, of the sodium thiosulphate solution required by the blank

V_1 = volume, in millilitres, of sodium thiosulphate solution required by the sample

and W = weight, in grammes, of sample taken

$$= \frac{\text{weight in grammes of sample in solution} \times \text{volume in millilitres, of solution taken.}}{900}$$

16.2 Method 2. Using sodium periodate

16.2.1 Reagents.

(i) Ethanediol.

(ii) Sodium periodate, 2 per cent (w/v) solution in water free from carbon dioxide.

(iii) Sodium hydroxide, approximately N solution.

(iv) Sulphuric acid. 10 per cent (w/v) aqueous solution (approx.)

(v) Hydrochloric acid, approximately N solution.

(vi) Sodium hydroxide, 0.05 N solution, accurately standardized, free from carbonates.

16.2.2 Procedure. Weigh 20 g of the soap to the nearest milligramme and dissolve in about 150 ml of water in a 250 ml beaker, precipitate the fatty acids by addition of a slight excess of the sulphuric acid solution and then allow the beaker and contents to stand, either overnight at room temperature or in a steam bath with frequent stirring, until the fatty acid layer is clear.

Transfer the aqueous phase to a 250 ml volumetric flask. Wash the fatty acid with several lots of water and add the washings to the flask. Dilute to the mark. Filter sufficient through a filter paper to fill a 100 ml volumetric flask. Transfer this exactly to a 500 ml conical flask and make just alkaline with the N sodium hydroxide solution. Add about 1 ml excess of the hydrochloric acid, boil gently for 3 minutes to expel carbon dioxide, stopper the flask with a soda-lime guard tube and allow to cool in a bath of cold water. When cool, wash down the sides of the flask with water free from carbon dioxide and adjust the pH of the solution to that used for the final titration by adding the 0.05 N sodium hydroxide solution. Add 25 ml of the periodate solution, insert the guard tube, swirl and allow the reaction to proceed for 30 minutes in the dark. Wash down the sides of the flask with water free from carbon dioxide, add 5 ml of ethanediol, swirl the flask and allow to stand in the dark for a further 20 minutes. Transfer the solution to a squat 500 ml beaker. Finally titrate the solution with 0.05N sodium hydroxide solution, using a pH meter, until the pH of the solution is 8.1. Carry out a blank test at the same time under exactly the same

conditions except that, while the pH value is adjusted to 8.1 before the addition of the periodate solution, the final titration is carried to an end point of pH 6.5 and not 8.1.

16.2.3 **Calculation.** Glycerol, per cent by weight

$$= \frac{1.1511\ (V_1 - V_2)}{W}$$

where V_1 = volume, in millilitres, of 0.05 N sodium hydroxide solution used in test,

V = The volume, in millilitres, 0.05 N sodium hydroxide solution used for blank

and W = weight, in grammes, of soap test portion taken.

Note. The standard sodium hydroxide solution should be standardized against potassium hydrogen phthalate.

17. DETERMINATION OF LOSS ON DRYING AT 100-105°C

In conjunction with the results of other analytical tests this method provides a check of the composition of the sample, but it does not give the true water content of soaps containing sodium silicate, sodium hydrogen carbonate, glycerol, perfume, ammonia, alcohol, carbolic acid or persalts, of soaps from linseed oil and other oxidizable oils. The water content of these soaps should be determined by the distillation method.

17.1 **Procedure.** Weigh, to the nearest milligramme, 3-4g of the prepared sample into a dry tared, porcelain or silica dish containing a glass pestle. Place the dish plus contents in an air oven maintained at 100-105°C. After drying has proceeded sufficiently, remove the dish, and by means of the pestle carefully crush all lumps, working the whole of the soap into a fine powder. Replace in the oven and dry to constant weight, i.e. a loss of not more than 3 mg in 1 hour's drying.

17.2 **Calculation.** Loss on drying at 100-105°C, per cent by weight

$$= \frac{100\ (W - W_1)}{W}$$

where W = weight, in grammes, of test portion taken

and W_1 = weight, in grammes, of test portion after drying.

18. DETERMINATION OF WATER (DISTILLATION METHOD)

Note. — In the presence of water-soluble volatile compounds the method is not applicable with modification. The amount of water lost by many of the compounds included in soaps will vary according to the temperature used for the distillation. The amount of water lost by hydrates by this method, will vary with the boiling point of the solvent and the transition point of the hydrate.

18.1 Reagent.

(i) Solvent. A suitable solvent for the purpose is light petroleum boiling range 100-120°C, or xylene. If polyphosphates are known to be present, the solvent should be light petroleum, boiling range 140-160°C.

18.2 Apparatus. The apparatus required comprises:

(i) Flask, round-bottomed and with a short neck and ground socket for connection to the receiver.

(ii) Receiver. (see Fig. 2a) Alternatively, in cases where emulsions of water and solvent form, the apparatus shown in Fig. 2b with the detachable receiver, may be used, and the tube and its contents removed and centrifuged before the reading is taken. The detachable receiver consists of a 15 ml centrifuge tube (graduated to 10 ml.). The actual dimensions of the centrifuge tube will depend on the centrifuge used. Flasks and receivers of appropriate capacities should be chosen for particular analysis.

(iii) Condensor, of the glass water-cooled type (see Fig. 2c).

(iv) Spray tube, as shown in Fig. 2d.

Clean the apparatus thoroughly with a mixture of potassium dichromate and sulphuric acid, rinse and dry before use.

18.3 Procedure. Weigh 10-20 g of sample into the flask of the distillation apparatus. Half fill the flask with solvent and add a few dry porcelain chips to regulate boiling. Attach the flask to the condenser and collecting tube and maintain the contents at the boil by means of a heating mantle, or other suitable form of heat, until the volume of water in the collecting tube no longer increases. Detach any globules of water from the condenser well by means of the spray tube shown in Fig. 2d. Allow the contents of the collecting tube to cool to the temperature of calibration of the apparatus and note the volume of water collected.

It is very important that the condenser and receiving tube should be carefully cleaned before each determination to remove any traces of fat.

18.4 **Calculation.** Water, per cent by weight $= \frac{100V}{W}$

where V = volume, in millilitres of water collected
and W = weight, in grammes, of test portion taken.

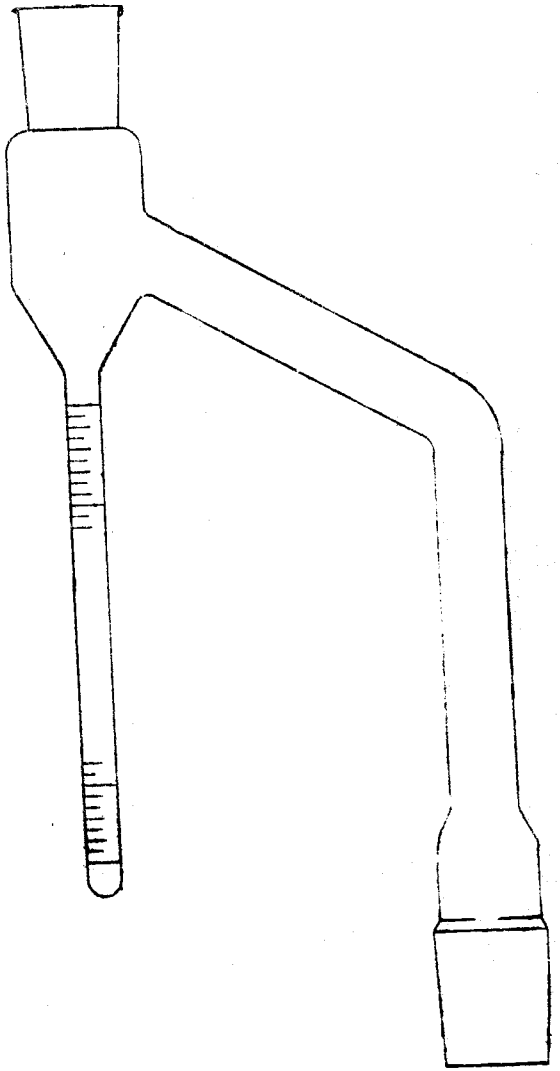

Fig. 2a. Receiver for distillation apparatus.

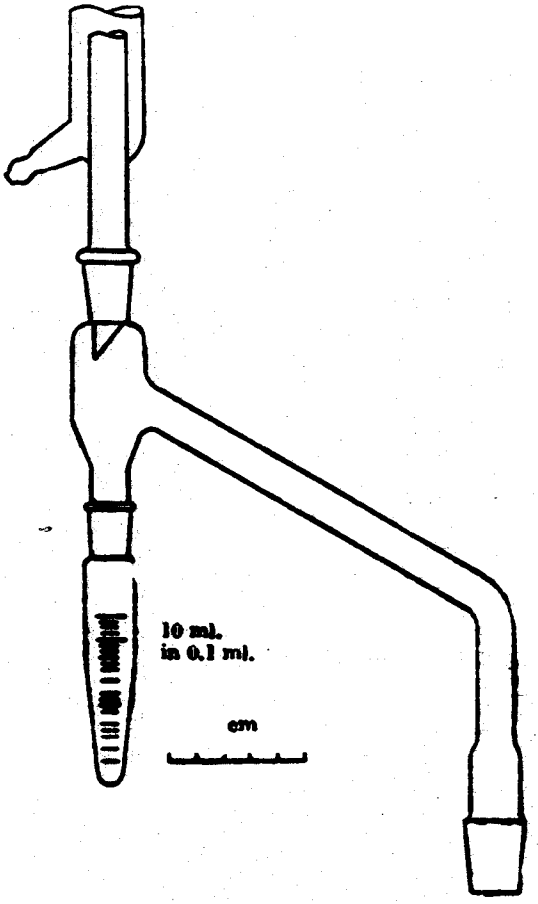

Fig. 2b. Alternative receiver for distillation apparatus.

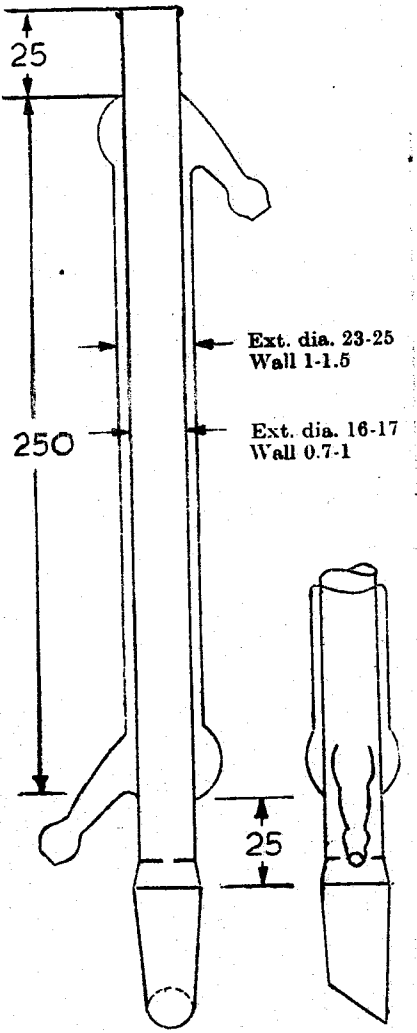

Fig. 2c. Condenser.

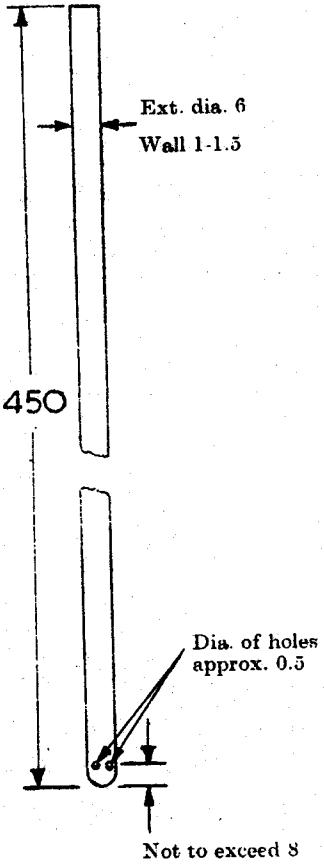

Fig. 2d. Spray tube.

(All dimensions are in mm)

AMD 36

AMENDMENT NO. 2 APPROVED ON 1981-01-29.

CS 27:1968 METHODS OF ANALYSIS OF SOAPS

Page 9 - Clause 3.5

In line 10 amend "0.22" to "0.022".

AMENDMENT NO. 3 APPROVED ON 2002 -08 - 08
TO CS 27 : 1968

METHODS OF ANALYSIS OF SOAPS

Clause **3.3 Reagents**
Line 3, delete 'N' and insert ' 0.5 M'
Line 6, delete 'N' and insert 'M'

Clause **4.1 Reagents**
Line 1, delete 'N' and insert 'M'
Line 2, delete 'N' and insert ' 0.5 M'

Clause **4.3 Calculation**
Line 4, delete 'N' and insert ' 0.5 M'
Line 6, delete 'N' and insert 'M'
Line 8, delete 'N' and insert '0.5 M'
Line 9, delete 'N' and insert 'M'
Line 17, delete 'N' and insert '0.5 M'

Clause **5.1 Reagents**
Line 2, delete 'N' and insert 'M' and delete 'o' after M and insert 'e'
Line 3, delete 'N' and insert 'M'
Line 4, delete 'N' and insert '0.5 M'

Clause **5.3 Calculation**
Line 4, delete 'N' and insert 'M'
Line 6, delete 'N' and insert '0.5 M'

Clause **6.1.1 Reagents**
Line 2, delete 'N' and insert 'M'
Line 3, delete 'N' and insert 'M'

Clause **6.1.3 Calculation**
Line 4, delete 'N' and insert 'M'

Clause **6.2.1 Reagents**
Line 5, delete 'N' and insert 'M'

Clause **6.2.3 Calculation**
Line 4, delete 'N' and insert 'M'

Clause **8.1.1 Reagents**
Line 2, delete 'N' and insert 'M'

Contd. 02

Clause **8.1.3 Calculation**

Line4, delete'N'and insert 'M'

Clause **8.2.1 Reagents**
Line 3, delete 'N' and insert 'M'
Line 7, delete 'N' and insert 'M'

Clause **8.2.2 Procedure**
Last paragraph, line 3, delete 'N' and insert 'M'

Clause **8.3.1 Reagents**
Line 1, delete 'N' and insert 'M'

Clause **11.1 Reagents**
Line 2, delete 'N' and insert 'M'
Line 3, delete 'N' and insert 'M'

Clause **11.3 Calculation**
Line 6, delete 'N' and insert 'M'

Clause **12.2 Reagents**
Line 2 delete 'N' and insert 'M'
Line 10, delete 'N' and insert 'M'
Line 12, delete 'N' and insert 'M'

Clause **12.4 Calculation**
Line 3, delete 'N' and insert 'M'
Line 5, delete 'N' and insert 'M'
Line 7, delete 'N' and insert 'M'

Clause **14.1.3.1 Reagents**
Line 8, delete 'N' and insert 'M'

Clause **14.2.1 Principle**
Line 11, delete 'N' and insert 'M'

Clause **14.2.2 Reagents**
Line 6, delete 'N' and insert 'M'

Clause **14.2.4 Procedure**
Paragraph 3, line 5, delete 'N' and insert 'M'
Paragraph 4, line 5, delete 'N' and insert 'M'

Contd. 03

Clause **14.2.5 Calculation**
Line 4, delete 'N' and insert 'M'

Clause **15.2.1 Reagents**
Line 5, delete 'N' and insert 'M'

Clause **15.2.3 Calculation**
Line 6, delete 'N' and insert 'M'
Line 8, delete 'N' and insert 'M'

Clause **16.1.1 Reagents**
Line 11, delete ' 0.1 N' and insert ' 0.02 M'
Line 12, delete 'N' and insert 'M'
Last paragraph, line 6, delete 'N' and insert 'M'

Clause **16.1.2 Standardization of sodium thiosulphate solution**
Line 10, delete 'normality' and insert 'molarity'

Clause **16.1.4 Calculation**
Line 2, delete 'N' and insert 'M'
Line 3, replace by the following :
' where M = molarity of sodium thiosulphate solution'

Clause **16.2.1 Reagents**
Line 4, delete 'N' and insert 'M'
Line 7, delete 'N' and insert 'M'
Line 8, delete 'N' and insert 'M'

Clause **16.2.2 Procedure**
Paragraph 2, line 6, delete 'N' and insert 'M'
Paragraph 2, line 13, delete 'N' and insert 'M'
Paragraph 2, line 20, delete 'N' and insert 'M'

Clause **16.2.3 Calculation**
Line 3, delete 'N' and insert 'M'
Line 5, delete 'N' and insert 'M'

BUREAU OF CEYLON STANDARDS

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