මෙය රාජ්‍ය භාෂාවෙන් වෙනම මුද්‍රණය කර ඇත.

ලංකා ප්‍රමිති 140 : 1972
CEYLON STANDARD 140 : 1972
විශ්ව දශම වර්ග කිරීම UDC 668.2

අශුද්ධ ග්ලිසරීන් (ග්ලිසරෝල්) පිළිබඳ ලංකා ප්‍රමිති පිරිවිතර

CEYLON STANDARD SPECIFICATION FOR CRUDE GLYCERINE (GLYCEROL)

ලංකා ප්‍රමිති කාර්යාංශය
BUREAU OF CEYLON STANDARDS

CEYLON STANDARD SPECIFICATION FOR CRUDE GLYCERINE (GLYCEROL)

C. S. 140 : 1972

Gr.13

BUREAU OF CEYLON STANDARDS
53, DHARMAPALA MAWATHA,
COLOMBO 3.

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.

This Standard does not purport to include all the necessary provisions of a contract.

BUREAU OF CEYLON STANDARDS
53, DHARMAPALA MAWATHA,
COLOMBO 3.

Telephone: **26055**
26054
26051

Telegrams: **"PRAMIKA"**

CEYLON STANDARD SPECIFICATION FOR CRUDE GLYCERINE (GLYCEROL)

FOREWORD

This Ceylon Standard Specification has been prepared by the Drafting Committee on Glycerine (Glycerol). 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 4th May, 1972.

Crude glycerine is one of the important products of the Oils and Fats Industry and is one of the non-traditional exports of Ceylon.

Crude glycerine, used mainly in the manufacture of various grades of refined glycerine, consists of the two grades, viz:

(a) Soap lye crude glycerine; and

(b) Hydrolyser (saponification) crude glycerine.

These two grades are being manufactured in Ceylon.

This Standard prescribes the requirements and the methods of test for the two grades of crude glycerine which are being manufactured. It does not cover the refined grades.

Dimensions and other characteristics in this specification are given in SI units with equivalent values in Imperial and/or technical metric units.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value observed or calculated expressing the result of a test, shall be rounded off in accordance with C.S. 102 : Ceylon Standard on Presentation of Numerical Values. The number of figures to be retained in the rounded off value shall be the same as that of the specified value in this standard.

In the preparation of this standard, the assistance obtained from the publications of the British Standards Institution and the Indian Standards Institution is acknowledged.

1. SCOPE

This standard prescribes the requirements and the methods of test for crude glycerine.

2. GRADES AND TYPES

The crude glycerine shall be classified into the following two grades and types.

Grade (i) Soap lye
- (a) Type I
- (b) Type II

Grade (ii) Hydrolyser (Saponification)

3. DESCRIPTION

3.1 Soap lye crude glycerine – The material shall be a viscous liquid prepared by evaporation of the purified lyes obtained as a by-product from the manufacture of soap by the boiling process.

3.2 Hydrolyser (Saponification) crude glycerine - The material shall be a viscous liquid prepared by evaporation of the sweet water obtained from the hydrolysis of oils and fats.

4. REQUIREMENTS

4.1 The soap lye and hydrolyser (Saponification) crude glycerine shall comply with the requirements given in columns (3) and (4) of Table 1 respectively and also in clauses 4.2 and 4.3.

4.2 The matter (organic non-glycerol, MONG when calculated by method described in Appendix F should not exceed 2.5 and 1.5 percent in soap lye and hydrolyser (saponification) crude glycerine respectively. If MONG does not exceed 2.0 and 1.0 percent respectively, there is no need to determine the non volatile organic residue [Table I (iv)].

TABLE I - REQUIREMENTS FOR SOAP LYE AND HYDROLYSER (SAPONIFICATION) CRUDE GLYCERINE

Serial No.	Characteristic	Requirement for Soap lye		Hydrolyser (Saponification)	Ref. to Appendix
		Type I	Type II		
(1)	(2)	(3)		(4)	(5)
(i)	Glycerol, percent by mass, min.	80.0	80.0	88.0	B
(ii)	Ash, percent by mass, max.	10.0	10.0	1.5	D
(iii)	Water content, percent by mass, max.	10.0	10.0	—	E
(iv)	Non-volatile organic residue, percent by mass, Max.	3.0	3.0	1.5	G
(v)	Arsenic, as As, parts per million, Max.	2.0	2.0	2.0	H
(vi)	Propane - 1:3 DIOL, percent (Trimethylene Glycol (TMG) max.)	0.5	0.5	0.5	I
(vii)	Chlorate, percent by mass, max.	1.0	nil	nil	P

Note 1 – Soap lye crude glycerol and hydrolyser (Saponification) crude glycerol do not necessarily fail to comply with this Ceylon Standard Specification because MONG exceeds 2.5 percent and 1.5 percent respectively.

Note 2 – If, after deducting the propane – 1:3 diol figure from the MONG figure, the balance still exceeds the non-volatile organic residue figure, volatile impurities other than propane – 1:3 diol may be present.

4.3 No sugar shall be detected when the material is tested by the method described in Appendix J.

5. TESTS

5.1 Tests shall be carried out as prescribed in the Appendices of this Standard. Reference to the relevent appendices are given in column 5 of Table 1 and in clauses 4.2 and 4.3.

6. SAMPLING

6.1 Representative samples of the material shall be drawn as prescribed in the Appendix A.

7.2 The containers shall be securely closed and legibly marked with the following information:

(a) Manufacturer's name; or and identification mark;

(b) Recognized trade mark, if any;

(c) Name and grade of the material;

(d) Masses of the material in the containers; and

(e) Batch number in code or otherwise to enable the lot of manufacture to be traced back from records.

APPENDIX A

SAMPLING

A-1 GENERAL

It is not possible to give instructions which will adequately cover all instances of sampling glycerine; frequently the procedure to be adopted will be dictated by the experience and judgement of the authority responsible for sampling. In many instances the methods given in the present standard will be applicable, but in other instances different procedures will need to be deviced to meet special circumstances.

There are, however, certain principles of a general character which should be followed to obtain samples as representative as possible.

A - 2 GENERAL PRECAUTIONS IN SAMPLING

A-2.1 The prevailing conditions should be surveyed before the sampling procedure is decided upon, e.g. by taking spot samples, by testing for the presence and condition of settled solids, noting stratification and other non-uniformity, etc.

A-2.2 Flow sampling should be used whenever possible.

A-2.3 For sampling glycerine, the sampling instruments may be made of copper, brass or bronze, but should be nickel plated.

A-2.4 All sampling apparatus shall be clean and dry when used.

A-2.5 Samples shall not be taken in an exposed place. The samples, the material to be sampled, the sampling instruments and the containers for samples shall be protected from adventitious contamination. The test samples shall be placed in suitable clean dry air-tight bottles.

A-2.6 On account of the very hygroscopic nature of glycerol, samples should be protected at all times from moisture and moist air. For the same reason sampling procedures should be designed to give the maximum protection to the glycerine.

A-2.7 To facilitate mixing, sample containers should not be more than two thirds full.

A-2.8 It is customary to divide the composite sample into at least three portions, each being stoppered and sealed by the sampler. One portion is for the purchaser, one for the vendor and one is kept for an independent analysis in case of dispute.

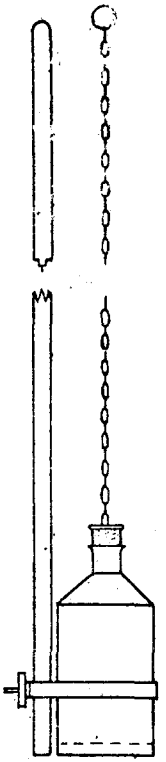

Fig. 1
Sampling Bottle
or Can

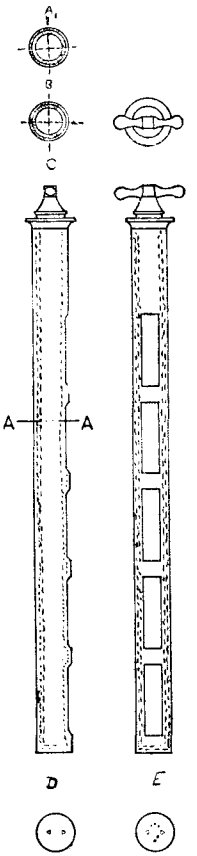

Fig. 2
Closed Type
Sampling Tube

A Closed
B Open
C Section A–A
D Bottom View - Open
E Bottom View - Closed

A-3 SAMPLING INSTRUMENTS

A-3.1 Sampling bottle or can (see Fig. 1)–This instrument is suitable for sampling large vessels and tanks of glycerine. It consists of a weighted glass or metal container with removable stopper to which is attached a suitable chain, pole or cord. This device is lowered to the various desired depths at which the stopper is removed and the container is allowed to fill.

A-3.2 Sampling Tubes - These instruments are suitable for sampling glycerine in drums and mobile tanks. The three recommended forms of sampling tubes are described in A-3.2.1 to A-3.2.3.

A-3.2.1 Closed type sampling tube, undivided (see Fig. 2) This instrument, also known as drum sampler, consists of two concentric metallic tubes closely fitted into each other throughout their entire length, so that one tube can be rotated within the other. Longitudinal openings of about one - third the circumference are cut in both tubes. In one position, the openings in the two tubes coincide; the sampling tube is open when in this position and admits the material. By turning the inner tube through an angle of 90°, it becomes a sealed container. The inner tube may have a diameter of 20 mm (0.80 in) to 40 mm (1.56 in) and is undivided along its length to serve as a single container.

The two concentric tubes are provided with ports at their bottom ends, so placed that the material contained in the instrument can be drained through them when the longitudinal openings coincide.

The length of the instrument should be such as to enable it to reach the bottom of the container being sampled.

The instrument is inserted closed, the material is admitted by opening it, and finally it is closed and withdrawn.

A-3.2.2 **Core sampler** - It consists of a hollow tube of approximately 50 mm (1.96 in) uniform internal diameter, and a length sufficient to take a sample through the entire depths of the liquid. The bottom is closed by a tight valve or cock which, when open, allows an unrestricted opening of the full size of the tube and which does not leak when closed. The valve is operated by a rod from the top and is so constructed that a sample can be taken within 10 mm (0.40 in) of the bottom of the drum or tank.

A-3.2.3 **Open type sampling tube** (see Fig. 3) - It is made of metal or thick glass, and may be of 20 mm (0.80 in) to 40 mm (1.56 in) diameter and 400 mm (15.76 in) to 850 mm (33.48 in) length. The upper and lower ends are conical and narrow down to 10 mm (0.40 in) to 15 mm (0. 60 in) diameter. Handling is facilitated by two rings at the upper end. For taking a sample, the instrument is first closed at the top with the thumb or a stopper and lowered until desired depth is reached. It is then opened for a short time to admit the material and finally closed and withdrawn.

A-3.3 **Dipper Sampler** (see Fig. 4) - This instrument is suitable for flow sampling. It consists of a beaker of approximately 500 ml (17.60 U. K. fl. oz.) capacity attached to a handle. This device may be used for collecting samples from the point of discharge, but great care must be taken to avoid contamination from mositure or moist air.

A-4 SAMPLE CONTAINERS

A-4.1 The samples shall be packed in clean dry glass bottles provided with suitable tight stoppers. Glass stoppers or new good quality velvet corks may be used but not rubber stoppers.

A-4.2 The sample container shall be sealed with wax in such a way that the contents and the label cannot be removed without breaking the imprint of the seal.

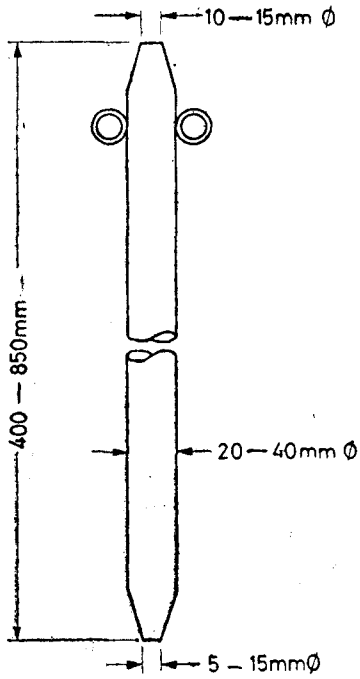

Fig. 3
Open Type Sampling Tube

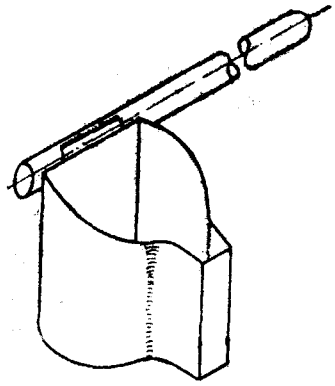

Fig. 4
Dipper Sampler

A-5 SCALE OF SAMPLING

A-5.1 **Lot** - All the containers in a single consignment of one grade of material drawn from a single batch of manufacture shall constitute a lot. If a consignment is declared to consist of different batches of manufacture, the batches shall be marked separately and the groups of containers in each batch shall constitute separate lots. Should the consignment not be uniform in quality, the parts of the consignment which appear to be similar may be collected together and each quality treated as a separate lot.

A-5.2 **Gross sample** - The general procedure for taking a gross sample is to draw a number of portions from the bulk quantity (see A-5.2.1) or a number of portions from all or several pakages (see A-5.2.2), and mix them thoroughly. Representative portions of the gross sample shall be transferred to air-tight containers of suitable size for the test samples as described under A-7.

A-5.2.1 **Gross sample from bulk quantities** – Gross sample from bulk quantities shall be drawn in quantities of not less than 20 kg (44 lb) per 20,000 kg (44,092 lb).

A-5.2.2 **Gross sample from small packages** – When sampling from drums, tins, bottles, etc. the packages from which the samples are drawn shall be selected at random from the lot. The following schedule is recommended for the number of packages to be sampled:

Number of packages in the lot	Number of packages to be sampled
1 to 4	All packages
5 to 100	At least 20 percent, with a minimum of 4 packages.
More than 100	At least 10 percent, with a minimum of 20 packages.

By agreement between the purchaser and the supplier, each package may be sampled. A minimum of 0.1 percent of the total quantity in the lot or 2 kg (4 lb) whichever is greater shall be drawn as the gross sample.

A-6 PROCEDURE FOR CRUDE GLYCERINE

A-6.1 **General** – The sampling of crude glycerine is sometimes made difficult by the presence of salt. The most satisfactory method of sampling is to take a flow sample during the transfer of the stock, or immediately after, before sedimentation of salt has taken place.

If it is necessary to sample after such separation has taken place, the thickness of the impenetrable salt layer at the bottom of the container may be estimated by means of a flat weight on a dipper tape. This bottom layer shall in such instances be sampled and accounted for separately.

A-6.2 **Crude Glycerine in Drums** – It is recommended that drums should be sampled before the salt has settled because it is almost impossible to obtain a correct proportion of salt after it has settled in the drums. If, however, the salt has settled in the drums, endeavour to soften any congealed soft layer by storing the drums in a warm place for several hours. Roll each drum through several revolutions to mix the contents, and test the condition of salt layer. If it has dispersed, proceed to sample by inserting the closed or open type sampling tube (see Figs. 2 and 3) through a close-fitting funnel fitted with a suitable washer so that the tube is automatically cleaned as it emerges. Discharge the samples into a receiving vessel by opening the ports.

If the salt layer has not dispersed, sample the glycerine above the salt layer in the manner and with the sampler discribed above. In this case arrangements should be made to sample the salt after transferring glycerine from the drums.

At the conclusion of sampling, prepare a gross composite sample by rapidly mixing the individual samples by stirring thoroughly with a clean wooden or stainless steel paddle and immediately transferring to clean dry air-tight bottles.

A-6.3 Crude Glycerine in Storage Tanks and Tank Wagons

A-6.3.1 Static tanks - It is not possible to lay down a standard method applicable in all instances, but the methods given here will usually be found suitable. If there is a hard impenetrable layer of salt which cannot be sampled at all, the thickness of this shall be measured but it shall not be finally accounted for until the tank is subsequently emptied. The material above this layer shall be sampled by either of the following two methods which are also suitable if there is no settled salt:

Method 1 Lower the core sampler vertically through the tank with the bottom valve or cock wide open, at a uniform rate slow enough to permit the tube to fill as it is lowered, that is, the tube should not be lowered faster than the glycerine can flow in so that the levels inside and outside the sampler are nearly equal at all times. This precaution must be carefully observed. Allow the core sampler to rest at the bottom of the tank for a short time before closing the valve or cook. Withdraw the core sampler slowly, wiping off glycerine clinging to the outside of the tube, and discharge into a mixing can. Repeat this operation if necessary to obtain a sample of sufficient size. Keep the mixing can covered at all times except when actually discharging samples into it or mixing the combined withdrawals. Rapidly mix the contents of the can by stirring thoroughly with a clean wooden or stainless steel paddle and immediately transfer to clean dry air-tight bottles.

Method 2 Take samples individually at uniformly spaced depths by lowering the sampling bottle (see Fig.1) to each chosen depth, opening it, filling and withdrawing. The individual portions so taken, including a portion as near to the tank bottom as possible, shall then be mixed in proportion to the quantities of material represented. Finally, sample the bottom layer of the glycerine by means of a core sampler or a broad, flat-bottomed, relatively shallow sampler open at the top (such as 150 mm diameter, 75 mm high). Mix this portion with that from the sampling bottle in proportion to the quantities of material represented by the samples. Mix the combined samples by stirring with a clean wooden or stainless steel paddle and immediately transfer to clean dry airtight bottles.

A-6.3.2 **During loading or unloading**–A dipper sampler (see Fig. 4) is recommended for sampling flowing glycerine at the discharge end of the pipe as the material enters or leaves the tank or tank wagon. The total gross sample to be accumulated should represent not less than 25 withdrawals of similar size, and spaced as uniformly as possible throughout the loading or unloading operation. Wipe the dipper sampler after each withdrawal or rinse it and dry before re-using, otherwise the remaining glycerine may absorb and thus include a significant quantity of moisture. Accumulate the withdrawals in a can large enough to permit thorough mixing. Keep the can tightly covered at all times except when actually discharging samples into it or mixing the combined withdrawals. Rapidly mix the contents of the can by stirring thoroughly with a clean wooden or stainless steel paddle and immediately transfer a portion of the glycerine to clean dry air-tight bottles.

A-7 TEST AND REFEREE SAMPLES

A-7.1 **Size of Test Sample** - The minimum size for each test sample shall be 750g (26.44 avoir, oz.).

A-7.2 **Preparation of Test Sample** - Normally, all the samples drawn as described under A-6 shall be put into a clean dry air-tight receptacle and mixed thoroughly. At least three uniform samples (test samples) shall be drawn therefrom. One test sample shall be sent to the purchaser and one to the supplier.

A-7.3 **Referee Sample** - The third test sample, bearing the seals of the purchaser and the supplier, shall constitute the referee sample to be used in case of dispute between the purchaser and the supplier.

A-8 TEST FOR ACCEPTANCE

A-8.1 **General** - It is advisable that all tests should be carried out in duplicate.

A-8.2 **Examination and Tests** - The purchaser may separately examine test samples of each of the separate packages (see A-5.2.2) for compliance with the requirements of the individual specification, or he may prepare, for the purpose of such examination and at any stage of the progress of the examination, a composite sample representing the whole of the consignment, by mixing the test samples.

A-8.3 **Criterion for Judgement** - If two or more qualities are examined from a consignment and if one or more of them do not comply with the requirements of the specification for that particular grade of crude glycerine, the purchaser shall have the right to accept only that portion which complies with the requirements, or accept or reject the whole of the consignment.

A-9 MARKING OF SAMPLE CONTAINERS

A-9.1 Each sample container after filling shall be sealed and marked with full details of sampling, the number of packages sampled, the date of sampling, and other particulars of the consignment.

A-9.2 A label bearing the particulars given under A-9.1 shall be attached to every sample container. A recommended form of label is given below:

Name and grade of material.....
Manufacturer or consignor.....
Lot Number.....
Size of consignment.....
Number of packages sampled.....
Place of sampling.....
Date of sampling.....
Signature of sampling officer.....
Brand name, if any.....

APPENDIX B

DETERMINATION OF GLYCEROL CONTENT

B-1 PRINCIPLE

Glycerol reacts with sodium periodate ($NaIO_4$) in acid aqueous solution to produce formaldehyde and formic acid, and the latter is used as a measure of the glycerol. Other polyhydric alcohols with three or more adjacent hydroxyl groups also produce formic acid and so interfere in the glycerol determination. The method cannot, therefore, be used directly on samples containing sugars (For the detection of sugar see Appendix J).

B-2 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used throughout.

B-2.1 Potassium hydrogen phthalate, buffer quality, dry.

B-2.2 Sodium periodate solution - Dissolve 60 g of sodium periodate, $NaIO_4$ complying with the specification given in Appendix L, in 500 ml of water, add 120 ml of 0.1N sulphuric acid solution and dilute to 1000 ml. Do not heat to dissolve the sodium periodate. If the solution is not

clear, filter through a sintered glass filter porosity 3. Store in a brown, glass-stoppered bottle, in the dark.

B-2.3 Ethanediol solution - Mix 1 volume of ethanediol, neutral and free from glycerol, with 1 volume of water.

B-2.4 Standard buffer solution, for standardisation of the pH meter (pH 4.0 at 20°C). Transfer 10.21 g of the buffer-quality potassium hydrogen phthalate (as B-2.1) to a 1000 ml one-mark volumetric flask. Dilute to volume with water and mix thoroughly.

B-2.8 Bromothymol blue indicator, 0.1 per cent solution in water. Dissolve 0.1 g of dry indicator in 16 ml of 0.01N sodium hydroxide solution by grinding the indicator with the alkali in a mortar. Transfer to a 100 ml one-mark volumetric flask, dilute to volume with water and mix thoroughly.

B-3 APPARATUS

B-3.1 Burette - 50 ml with a tolerance on capacity of ± 0.05 ml.

B-3.2 Magnifying lens to permit reading the burette to 0.01 ml.

B-3.3 Pipette - 50 ml, bulb pattern, with a tolerance on capacity of ± .04 ml.

B-3.4 Variable-speed electric stirrer with glass stirrer blade (A magnetic stirrer is also suitable).

B-3.5 pH meter with glass electrode.

B-3.6 Weighing pipette of the Lunge-Rey pattern, with an enlarged aperture if required, or weighing bottle.

B-3.7 Beakers, 600 ml squat.

B-4 PREPARATION OF THE SAMPLE

Careful preparation of the sample is necessary for an accurate analysis. Warm and thoroughly mix samples containing sediment or suspended matter to ensure uniform distribution. Some sediment tends to cling to the bottom of the container and the high viscosity of cold glycerol retards rapid dispersion. Any mixing procedure which will secure thorough distribution is satisfactory. Take care to avoid absorption or loss of water by the sample.

B-5 PROCEDURE

Using the weighing pipette or weighing bottle, transfer into a beaker a weighed account, within the limits given by the formula

$$\frac{41 \pm 9}{P} \text{ grammes.}$$

where **P** is the expected percentage of glycerol in the sample.

When the glycerol content is unknown, weigh the amount specified for 100 percent glycerol, and from the results of this test select the proper size of sample.

Dilute the sample to approximately 50 ml with water. Add 5-7 drops of bromothymol blue indicator to the solution and acidify with 0.2N sulphuric acid solution to a definite green or greenish-yellow colour.

Note : If the glycerol analysed contains more than 0.1 percent of carbonate alkalinity, determined in the manner described in Appendix M (Test 3) and expressed as Na_2O, add 0.2N sulphuric acid solution until the pH is 3.0 or lower, heat to boiling and cool to room temperature. Neutralize with 0.05N sodium hydroxide solution using bromothymol blue as indicated below.

Neutralize the solution carefully with 0.05N sodium hydroxide solution to a blue free of green colour. If the colour of the solution interferes with the detection of the colour change of the indicator,

or if the sample contains an appreciable amount of buffering material, use the pH meter and adjust to pH 8.1 ± 0.1.

Note : In some instances, buffering action may be sufficiently great to prevent good reproducibility or results.

Prepare a blank containing 50 ml of water, but no glycerol, and treat in the same manner as the sample, using the indicator to adjust the pH before addition of sodium periodate solution.

Pipette 50 ml of sodium periodate solution into the sample and the blank, swirl gently, cover each beaker with a clock glass, and allow to stand for 30 minutes at room temperature (not higher than 35°C) in the dark. At the end of this period add 10 ml of ethanediol solution, swirl gently and allow to stand at room temperature (not higher than 35°C) in the dark for 20 minutes.

Dilute to about 300 ml and titrate the solutions with the 0.125N sodium hydroxide solution, using the pH meter to determine the end point, which is pH 6.5 ±0.1 for the blank and 8.1±0.1 for the sample. Read the burette to 0.01 ml.

Note 1: Titration of the blank to pH 6.5 and of the test solution to pH 8.1 amounts to applying a correction of about 0.3 per cent of glycerol expressed on 100 per cent glycerol. This is necessary because of the difference in equivalence point caused in one case by the presence of glycerol.

Note 2: If a pH meter is not available, an alternative to the method is to use phenol red indicator (0.05 per cent aqueous solution) in place of bromothymol blue. Titrate the blank and test solution to the colour change of the indicator (yellow to red). Add 0.3 percent (expressed on 100 per cent glycerol) to the observed glycerol result. This is not a reference method.

Note 3: The presence of a sufficient excess of sodium periodate in a given test can be cheked as follows:

Test the sample using three-quarters of the sample weight used in the original test. This can be done when running

duplicate tests by weighing one sample approximately three-quarters of the weight of the other. If the analysis of the smaller sample agrees with that of the larger sample there is a sufficient excess of sodium periodate in both cases. If the analysis of the smaller sample shows a glycerol content higher by more than experimental error, there was not sufficient excess of sodium periodate for the complete oxidation of the larger sample, and it is necessary to carry out another test using a smaller sample.

Note 4: It is advisable to make an occasional check on the procedure by the use of a 'standard glycerol'. The object of this test is to check whether a mistake is being made in procedure or whether one of the reagent additives is faulty. The 'standard glycerol' may be prepared as follows:

Subject chemically pure glycerol made from glyceride oils and fats to fractional vacuum distillation at an absolute pressure of 0.1 mm Hg and a temperature not higher than 150° C to give a first distillate fraction (about 15 per cent), a large middle fraction (about 70 per cent), and a residue (about 15 per cent). Examine these fractions after dilution to about 90 per cent with water, for water content (by Karl Fischer method described in Appendix E), specific gravity described in Appendix O, and glycerol by the sodium periodate method described herein. The glycerol is standard when the specific gravity and water content of the three fractions show the same relationship within the experimental limits of a spread of 0.2 per cent and the same glycerol content by the sodium periodate method when allowance is made for the water content. (Possible impurities such as propane - 1:3 - diol and diglycerol give a sodium periodate figure and, if present in one or two fractions, show a divergence between the water and glycerol relationship in the fractions). If the three fractions do not correspond in the above three respects, re-distil the middle fraction in the same manner as previously and examine the fraction thus obtained. Repeat this procedure until the three fractions correspond in the three respects given above.

This 'standard glycerol' is not intended to be used for the standardisation of the sodium hydroxide solution.

B-6 CALCULATION

$$\text{Glycerol, per cent by mass} = \frac{1.151\ (T_1 - T_2)}{m}$$

where T_1 = volume, in millilitres of 0.125N sodium hydroxide solution required for sample,

T_2 = volume, in millilitres of 0.125N sodium hydroxide solution required for blank,

and m = mass, in grammes, of glycerol taken for test.

APPENDIX C

DETERMINATION OF ACIDITY OR ALKALINITY

Note: It is advisable that all tests should be carried out in duplicate.

C-1 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

C-1.1 Sodium hydroxide, O.1N solution.

C-1.2 Hydrochloric acid, O.1N solution.

C-1.3 Phenolphthalein indicator – Dissolve 1 g of phenolphthalein in 200 ml of 95 per cent (v/v) ethanol*. Add C.5N sodium hydroxide solution cautiously until a faint pink colour persists.

C-2 PROCEDURE

Weigh accurately about 100 g of the well mixed sample into a 500 ml conical flask and add 150 ml of the water. Determine

* Ethanol may be replaced by industrial methylated spirits of equivalent strength.

as indicator.

C-3 CALCULATION

(i) Acidity, per cent as Na_2O equivalent $= \frac{0.31 \ T_1}{m}$

(ii) Alkalinity, per cent as Na_2O $\frac{0.31 \ T_2}{m}$

where, T_1 = volume, in millilitres of O.1 N sodium hydroxide required.

T_2 = volume, in millilitres of O.1 N hydrochloric acid required.

and m = mass, in grammes, of sample taken.

APPENDIX D

DETERMINATION OF ASH OF CRUDE GLYCEROL

Note: It is advisable that all tests should be carried out in duplicate.

D-1 APPARATUS

Platinum dish, top diameter approximately 75 mm base diameter approximately 63 mm and depth approximately 25mm. The bottom of the dish is joined to the sides by a curve and not a sharp angle.

D-2 PROCEDURE

Accurately weigh about 2 g of soap lye crude glycerol or about 5 g of hydrolyser crude glycerol in the platinum dish and evaporate over an Argand burner or other source of heat giving a low flame temperature. Continue heating until the sample is completely charred, i. e. until all visually detectable change in the sample has ceased. Transfer the dish to a muffle furnace

maintained at 750°C, with ventilator fully closed. After heating at 750°C for ten minutes, transfer the dish to a desiccator, allow it to cool and weigh the residue.

D-3 CALCULATION OF RESULTS

$$\text{Ash, per cent, by mass} = \frac{100\ m_1}{m}$$

where m_1 = mass, in grammes, of residue,

and m = mass, in grammes, of sample taken.

APPENDIX E

DETERMINATION OF WATER

Note: It is advisable that all tests should be carried out in duplicate.

E-1 OUTLINE OF METHOD

The Karl Fischer reagent is standardised by titrating it against a weighed amount of sodium acetate trihydrate of known moisture content, the trihydrate dissolving in the reagent during titration. A weighed amount of the sample is tested in the same way.

E-2 REAGENTS

The reagents used shall be of a recognized analytical reagent quality.

E-2.1 Sodium acetate trihydrate, of known water content (usually about 39 per cent) determined by drying to constant weight in an oven at 130°C.

E-2.2 Karl Fischer reagent, having a water equivalent of between 0.003 and 0.004 g/ml, prepared as described below.

(i) Methanol, anhydrous

(ii) Pyridine

(iii) Iodine, resublimed

(iv) Sulphur dioxide, liquid, from glass siphon.

Measure 800 ml of the methanol into a dry 2 litre flask fitted with a two-hole rubber stopper through which an inlet tube passes reaching nearly to the bottom of the flask. Add 90 g of iodine. Shake to dissolve the iodine, then add 142 ml of pyridine. Weigh the flask with its fittings and contents. Connect the inlet tube to the siphon of sulphur dioxide and allow the gas to pass into the mixture, with frequent shaking, until the total mass of the flask and its contents is increased by 40 g. Any escaping sulphur dioxide is trapped in a wash bottle containing anhydrous methanol. Allow the mixture to stand for 24 hours. Finally, transfer the prepared reagent to the appropriate burette reservoir bottle. The water equivalent of the Karl Fischer reagent thus prepared will be about 0.0035 g/ml.

E-3 APPARATUS

The apparatus required, a suitable form of which is shown in Figs. 5, 6, 7 comprises the following items:

E-3.1 Titration vessel, a conical flask, working capacity 100 ml protected with a guard tube filled with calcium chloride or other suitable desiccant. The neck terminates in a suitable airtight detachable joint fitted to accommodate a burette jet which is extended to a suitable length. Two nickel-chrome electrodes extending nearly to the bottom of the flask are inserted through the seal, or, alternatively two platinum electrodes are sealed in at the base of the flask.

E-3.2 Burette, 50 ml capacity, fitted with guard tube filled with calcium chloride or other efficient desiccant.

E-3.3 Reagent reservoir, connected to the burette and protected with a drying tower filled with calcium chloride or other efficient desiccant.

E-3.4 An electrical circuit, consisting of dry cells, resistances and meter as shown in Fig. 7.

E-3.5 Magnetic stirrer, with rotor 18 mm (0.75 in) long, polythene-covered, or other similar device.

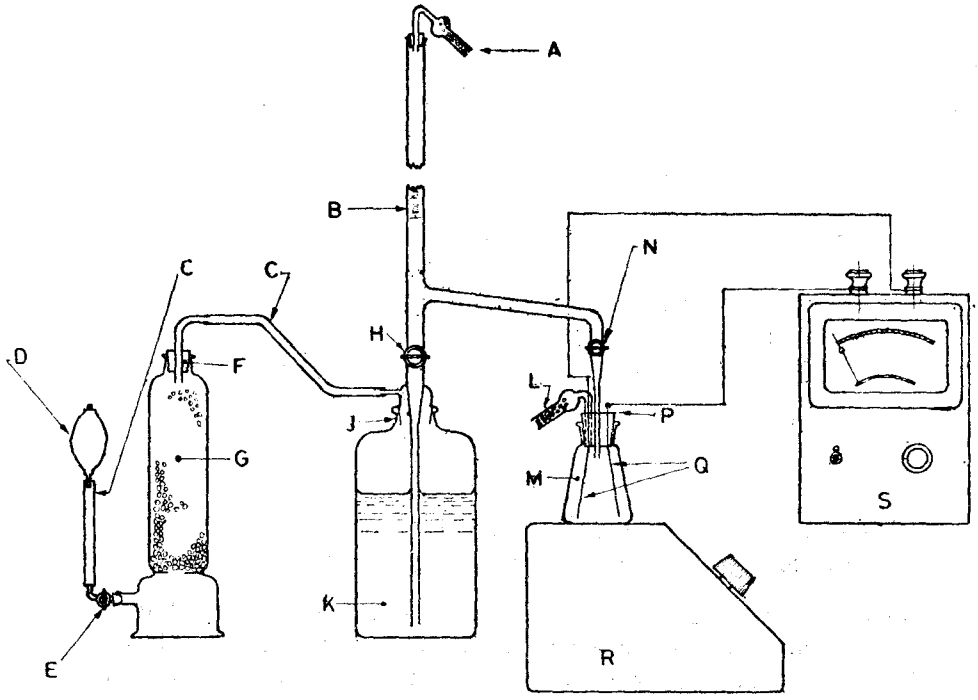

Fig. 5

General Arrangement

A Calcium chloride drying tube.

B 50 ml burette with B 24 ground glass joint.

C Rubber tubing.

D Rubber bellows.

E 2mm stop cock.

F Rubber stopper.

G Calcium chloride drying tower 200 mm × 40 mm internal.

H 4 mm stop cock.

J B 24 ground joint.

K Fisher reagent.
1 l bottle.

L Calcium chloride drying tube.

M 100-ml flask
S Electrical end-point detector (range

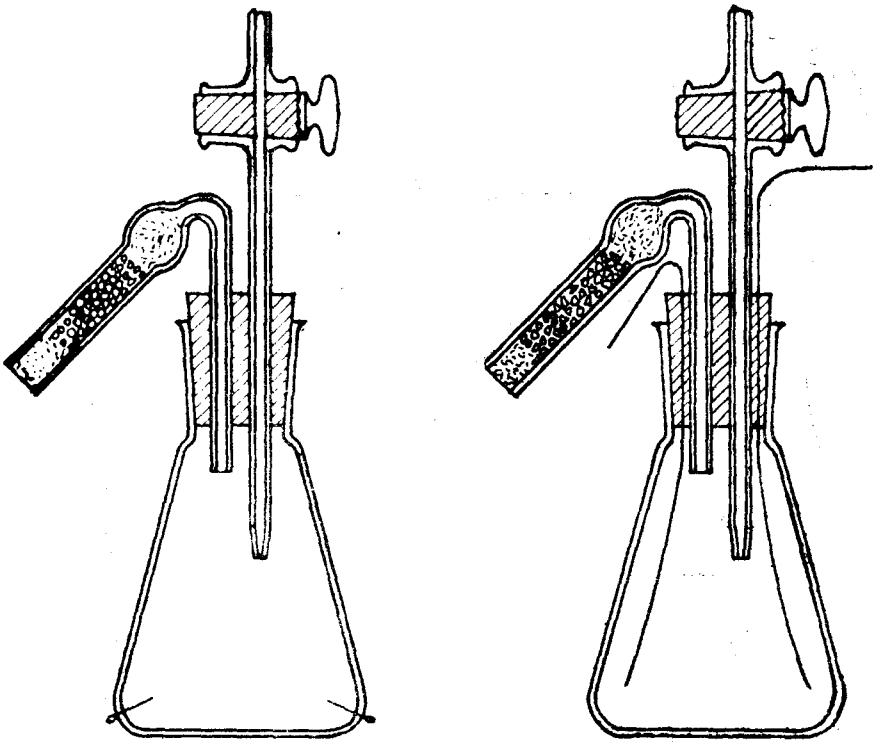

Fig. 6
Titration Vessels

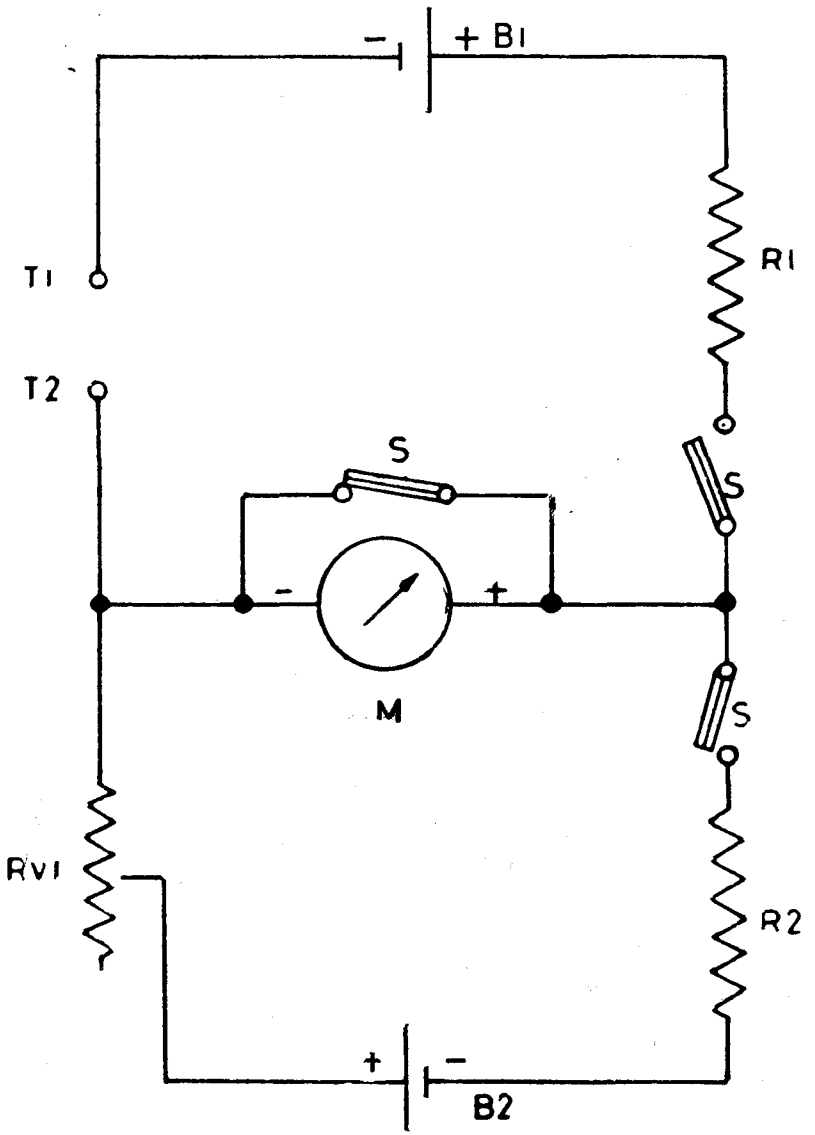

Fig. 7
Circuit diagram for end-point detector

B1	1.5 V 'S' type dry cell	R2	10 000Ω ¼W carbon resistor
B2	1.5 V 'S' type dry cell	RV1	½MΩ ¼W potentiometer carbon
S	Change over switch	M	4 in rectangular meter F. S. D. 5μA for horizontal use
R1	10 000Ω ¼W carbon resistor	T1 T2	B type terminals

E-4 PROCEDURE

E-4.1 Standardisation of Karl Fischer reagent - Weigh accurately 0.3 - 0.4 g of the sodium acetate trihydrate and transfer it to the titration vessel, which has been previously dried in an oven at above 95° C. Place the magnetic stirrer in the vessel and attach this to the burette containing the Karl Fischer reagent. Run in sufficient reagent to make electrical contact with the electrodes (about 10 ml) and start the magnetic stirrer. Adjust the end-point detector to give a reading of 0 - 2 micro-amps and continue the titration until a further drop of reagent causes the needle of the detector to be fully deflected and to remain so for 30 seconds. From the mass of sodium acetate trihydrate and the volume of Karl Fischer reagent used calculate the water equivalent of the Karl Fischer reagent as grammes of water per cubic centimetre of reagents.

E-4.2 Determination of water in glycerol - Transfer to a tared titration vessel sufficient glycerol to give a titration of 30 - 40 ml of Karl Fischer reagent and reweigh (2 - 3 g of crude glycerol). Add the rotor of the magnetic stirrer and complete the titration as described in the standardisation.

$$\text{Water content, per cent, } = \frac{100\ EV}{m}$$

where E = water equivalent, in grammes, per millilitre of the Karl Fischer reagent,

V = volume, in millilitres of Karl Fischer reagent used

If desired, the magnetic stirrers may be dried, cooled and weighed with the titration vessels, in which case each should be dried in the vessel and be part of its tare, it having been ascertained that the plastics coating of the stirrer is not affected by the temperature of drying.

Note 2- The Karl Fischer reagent should be drained into the reservoir from the burette after completing a run of titrations. The burette should be flushed with the reagent several times before use by pumping the solution up to the top of the burette and letting it run back into the reservoir. The side arm of the burette should be flushed by letting a little of the reagent run to waste.

Note 3- Effect of alkali :

The usual reaction between water and Karl Fischer reagent can be simplified to

$$H_2O + I_2 + SO_2 + CH_3OH = 2HI + HSO_4CH_3$$

followed by salt formation with pyridine. Note the difference from the reaction between iodine and sulphur dioxide in aqueous solution.

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$$

(Bunsen, Annalen, 1853, 86, 265).

Smith et al have shown that the alkali metal oxides, hydroxides, and carbonates react similarly.

(J. Amer. Chem. Soc. 1941, 63, 2927).

Alkalinity in crude glycerol will therefore lead to fictitiously high results for water content, when titrated with Karl Fischer reagent. The correction necessary may be calculated as follows:

H_2O equivalent of alkalinity = 0.58 A

where A is the alkalinity to phenolphthalein, determined and calculated as in Appendix C.

APPENDIX F

CALCULATION OF MATTER (ORGANIC) NON-GLYCEROL (MONG)

MONG; per cent by mass = 100 - (G + A + m)

where G = the percentage, by mass of glycerol determined by the method described in Appendix B.

A = the percentage, by mass of ash determined by the method described in Appendix D.

and m = the percentage, by mass of water determined by the method described in Appendix E.

APPENDIX G

DETERMINATION OF TOTAL RESIDUE AT 160°C AND CALCULATION OF NON-VOLATILE ORGANIC RESIDUE AT 160°C

Note: It is advisable that all tests should be carried out in duplicate.

G-1 REAGENT

The reagent used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

Hydrochloric acid, N solution,
or sodium carbonate, N solution.

G-2 APPARATUS

G-2.1 One - mark volumetric flask, 100 ml.

G-2.2 Pipette, 10 ml.

G-2.3 Evaporating dish, diameter at base about 63.0 mm (2.5 in) and depth 12.5 mm (0.5 in). The bottom of the dish is joined to the sides by a curve and not a sharp angle (otherwise pockets of liquid are formed which slow down the evaporation rate). The bottom is flat and of uniform thickness.

G-2.4 Thermostatically controlled oven, capable of maintaining 160° C when a current of air is blown in.

For this purpose the oven is fitted with a chimney, and there is a vent hole of about 25 - 50 mm (1.00 - 1.96 in) diameter in the door or sides. Two perforated metal tubes of 12.5 mm (1.492 in) internal diameter are fitted horizontally in the oven in such a way as to permit air to be blown across the surface of the shelf which carries the dish. (A suitable arrangement is shown in Fig.8). As a source of air, any small blower with a capacity of about 21.3 L (0.752 cu. ft.) per minute at a pressure of about 48kN/m^2 (0.49 kgf/cm^2) (7.0 lbf/in^2) suitable.

G-3 PROCEDURE

Weigh accurately 10 $\pm$ 0.05 g of the sample into the 100 ml flask and dilute with water. To prevent loss of organic acids, adjust the sample to an alkalinity of 0.2 per cent (as Na_2O) by adding the appropriate volume of the hydrochloric acid or sodium carbonate solution, calculated as in G 3.1, G 3.2 or G 3.3 below. To avoid formation of polyglycerols it is essential that this alkalinity shall not be exceeded.

Note: In the following calculation the percentage of total free alkali as Na_2O is defined as the sum of the percentage

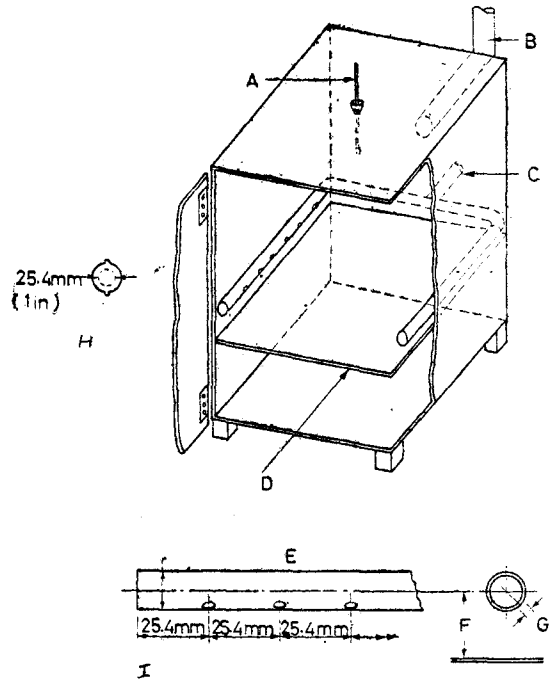

Fig. 8

Diagram of oven fittings for the determination of total residue in crude glycerol

A Thermometer
B Chimney
C Air inlet
D Tray for glycerol dishes
E 12.7 mm (0.500 in) pipe
F 25.4 mm (1 in) tray
G 3.175 mm (0.1248 in) hole at 45°C
H Swivelling cover plate in centre of door.
I 3.175 mm (1/8 in) air holes at 25.4 mm intervals along entire length of pipe inside the oven.

(25.4 mm = 1.000 in.)

of free caustic alkali as Na_2O (see Appendix M, Method 1) and the percentage of carbonate alkalinity as Na_2O (see Appendix M, Method 3).

C-3.1 If the sample is alkaline, and contains more than 0.20 per cent of total free alkali as Na_2O (defined as above), the volume, V_1, of N hydrochloric acid solution to be added

$$= \frac{C+H}{0.31} - 0.65 \text{ ml}$$

G-3.2 If the sample is alkaline, and contains less than 0.20 per cent of total free alkali as Na_2O (defined as above), the volume, V_2, of N sodium carbonate solution to be added

$$= 0.65 - \frac{C+H}{0.31} \text{ ml}$$

G-3.3 If the sample is neutral, the volume of N sodium carbonate solution to be added

$$= 0.65 \text{ ml.}$$

G-3.4 If the sample is acid, the volume, V_3, of N sodium carbonate solution to be added

$$= \frac{A}{0.31} + 0.65 \text{ ml}$$

where A = percentage of acidity, as Na_2O equivalent,
C = percentage of carbonate alkalinity, as Na_2O,
H = percentage of caustic alkalinity, as Na_2O.

Fill the flask to the mark with water, mix the contents and pipette 10 ml into the weighed evaporating dish.

When crude glycerol is abnormally high in organic residue, evaporate a smaller quantity so that the weight of organic residue is in the range of 30 - 40 mg.

Evaporation of the glycerol : A long evaporation period leads to the formation of polyglycerols and erratic results are obtained. This error can be avoided by passing a stream of air over the dish whilst it is in the oven.

Place the dish on a water bath or on top of the oven until most of the water has evaporated; from this stage carry out the rest of the operation in the oven. The dish should be placed on a piece of asbestos-type board and the bulb of the control thermometer kept level with the dish and close to it.

With the equipment described, the glycerol may be evaporated at 160° C in about one hour without risk of polymerization. It is recommended that the current of air be maintained during the whole period of evaporation, the vapours being allowed to escape through the chimney. When only slight or no vapours are seen to be coming off, remove the dish and allow it to cool. On this stage being reached no further air blowing is necessary.

Add 0.5 - 1.0 ml of water, and by a rotary motion bring the residue wholly or nearly into solution. Allow the dish to remain on the water bath until the excess water has evaporated, and the residue is in such a condition that on returning it to the oven at 160° C spurting will not occur. Usually two or three hours are required.

Allow the dish to remain in the oven, carefully maintaining the temperature at 160° C during exactly one hour, then remove it and cool. Again treat the residue with water in the manner described and evaporate the water as before. Subject the residue to a second baking for exactly one hour, after which allow the dish to cool for a set period of time (which is to be observed in all subsequent cooling periods) in a desiccator over sulphuric acid and weigh. Repeat the treatment with water, baking, cooling etc., until a constant loss of 1 - 1.5 mg per hour is obtained.

G-4 CALCULATION OF TOTAL RESIDUE AT 160°C

G-4.1 If the sample is alkaline and contains more than 0.20 per cent total free alkali as Na_2O.

(i) When the carbonate alkalinity is less than 0.20 per cent as Na_2O, the remainder being free caustic alkalinity.

Total residue at 160° C = 100 (m – 0.0019 V_1) per cent.

(ii) When all the alkalinity is due to carbonate:

Total residue at 160° C = 100 (m – 0.0006 V_1) per cent.

(iii) When the carbonate alkalinity, exceeds 0.20 per cent as Na_2O and free caustic alkalinity is also present:

Total residue at 160° C = 100 (m – 0.0018 C –0.0060 H + 0.0004) per cent.

G-4.2 If the sample is alkaline and contains less than 0.20 per cent total free alkali as Na_2O:

Total residue at 160° C = 100 (m – 0.0053V_2) per cent.

G-4.3 If the sample is neutral:

Total residue at 160° C = 100 (m – 0.0034) per cent.

G-4.4 If the sample is acid:

Total residue at 160° C = 100 (m – 0.0022 V_3 – 0.0020) per cent.

where C = percentage carbonate alkalinity, as Na_2O,

H = percentage caustic alkalinity, as Na_2O,

V_1 = volume, in millilitres of N hydrochloric acid solution added as under G. 3. 1,

V_2 = volume, in millilitres of N sodium carbonate solution added as under G. 3. 2,

V_3= volume, in millilitres of N sodium carbonate solution added as under G. 3. 4,

and M = mass, in grammes, of total residue.

Calculation of non-volatile organic residue at 160° C,

Non-volatile organic residue at 160° C percent by mass (A–B)

where A = total residue at 160° C percent by mass, as determined above

and B = ash, percent by mass, as determined in Appendix D.

Note: Alkaline salts of organic acids are converted to carbonates on ignition and the CO_3 radical thus derived is not included in the non-volatile organic residue.

APPENDIX H

DETERMINATION OF ARSENIC

Note: It is advisable that all tests should be carried out in duplicate

H–1 REAGENTS

The reagents used shall be of a recognized analytical reagent quality, and shall be free from arsenic. Distilled water, or water of at least equal purity, shall be used.

H–1.1 Granulated zinc.

H–1.2 Hydrochloric acid, concentrated, d = 1.18.

H–1.3 **Arsenous oxide** - Dissolve 0.132 g of arsenous oxide (As_2O_3) in 10 ml of N sodium hydroxide solution. Neutralize the alkali by adding 10 ml of N sulphuric acid solution and dilute to 100 ml in a volumetric flask. Dilute, as required, 1 ml of this solution to 1000 ml with distilled water. This solution contains 1 μg of arsenic per millilitre. This solution is unstable and should be freshly prepared.

Warning: Do not measure solution containing arsenic by means of a pipette filled by suction with the mouth: use a burette or other dispensing device.

H-1.4 **Stannated hydrochloric acid** - Dilute 60 ml of the hydrochloric acid with 20 ml of water, add 20 g of tin, heat gently until gas ceases to be evolved and add sufficient water to produce 100 ml allowing the undissolved tin to remain in the solution. To 1 ml of this stannous chloride add 100 ml of the hydrochloric acid.

H-1.5 **Bromine** - 30 per cent (m/v) solution. Dissolve 30 g of bromine and 30 g of potassium bromide in water and make up to 100 ml.

H-1.6 **Lead acetate papers** - Soak pieces of thin white filter paper, 100 x 50 mm, in 10 percent (m/v) lead acetate solution, and dry.

H-1.7 **Mercuric chloride papers** - Soak pieces of smooth white filter paper, not less than 25 mm in width, in a saturated solution of mercuric chloride in water, press to remove superfluous moisture, and dry at about 60° C in the dark. The grade of the filter paper shall be such that the mass in grammes per square metre is between 65 and 120; the thickness in millimetres of 400 papers shall be approximately numerically equal to the weight in grammes per square metre.

Note:- The mercuric chloride papers should be stored in a stoppered bottle in the dark. Papers which have been exposed to sunlight or to the vapour of ammonia afford a lighter coloured stain or no stain at all, when employed in the arsenic test.

H-2 APPARATUS

A wide-mouthed bottle, capacity about 120 ml is fitted with a rubber bung through which passes a glass tube. The latter, made from ordinary glass tubing, has a total length of 200 mm and an internal diameter of exactly 6.5 mm (external diameter about 8 mm) and is drawn out at one end to a diameter of about mm; a

hole not less than 2 mm in diameter is blown in the side of the tube, near the constricted part. The tube is passed through the bung so that, when the bung is inserted in the bottle containing 70 ml of liquid, the constricted end of the tube is above the surface of the liquid and the hole in the side is below the bottom of the bung. The upper end of the tube is cut off square, and is ground smooth.

Two rubber bungs (about 25 x 25 mm), each with a hole bored centrally and true, exactly 6.5 mm in diameter, are fitted with a rubber band or spring clip for holding them tightly together. Alternatively the two bungs may be replaced by any suitable contrivance satisfying the conditions described below.

H-3 PROCEDURE

Roll a strip of the lead acetate paper to form a cylinder 100 mm in length, and place it in the glass tube so that the upper end is not less than 25 mm below the top of the tube. Then insert the upper end of the tube into the narrow end of one of the pair of rubber bungs so that the ground end of the tube is flush with the larger end of the bung. Place a piece a mercuric chloride paper flat on the top of the bung and the other bung over it. Secure by means of spring clips, in such a manner that the bores of the two bungs meet to form a true tube of 6.5 mm diameter interrupted by a diaphgram of mercuric chloride paper.

Weigh accurately about 10 g of the sample into the wide-mouthed bottle, add 10 g of zinc, 50 ml of water and 10 ml of stannated hydrochloric acid and then quickly place the prepared glass tube in position. Allow the action to proceed for 40 minutes at a temperature of not higher than 40° C.

At the same time produce standard stains of arsenic by introducing 5 ml of the arsenic oxide solution into a second wide-mouthed bottle and 10 ml of the arsenous oxide solution into a third wide-mouthed bottle. Add to each of these 10g of zinc, 50 ml of water, and 10 ml of stannated hydrochloric acid and quickly place prepared glass tubes in position, allowing the action to proceed for 40 minutes at a temperature not higher than 40° C.

Compare in daylight the yellow stain which is produced on the mercuric chloride paper, if arsenic is present in the glycerol, with the standard stains produced from the known quantities of the arsenous oxide solution. From the intensity of the stain produced by the glycerol sample make an estimate of the amount which would be needed to produce exactly comparable stains. If the stain is greater in intensity than the 10 ml standard stain then a less amount of glycerol should be used and, conversely, if the stain is less intense than the 5 ml standard stain, then an amount greater than 10 g of glycerol should be used. Finally evaluate the arsenic content by using the indicated amount of glycerol to produce an exactly matching stain.

Note: When a glycerol contains sulphides, sulphites or thiosulphates in such amount as to vitiate the arsenic test, heat a weighed amount of the sample with bromine water and then make to a convenient volume from which a known aliquot portion is used for the arsenic determination.

H-4 CALCULATION

(i) If the sample matches the 10 ml standard stain,

$$\text{Arsenic, p.p.m., as As} = \frac{10}{m}$$

(ii) If the sample matches the 5 ml standard stain,

$$\text{Arsenic, p.p.m., as As} = \frac{5}{m}$$

where m = mass, in grammes, of sample taken.

APPENDIX I

METHOD FOR THE DETERMINATION OF PROPANE-1:3 DIOL [TRIMETHYLENE GLYCOL (TMG)]

I-1 PRINCIPLE

As propane - 1:3-diol and glycerol have widely different vapour pressures at a given temperature, they are easily and directly separated by gas-liquid chromatography.

A polar stationary phase is necessary to minimize absorption on the inert support, with consequent trailing of the elution peaks. A polyester is recommended as it gives satisfactory separation and is stable at the operating temperature. Any transesterification that may take place between the glycerol or propane-1:3 - diol and the stationary phase is too slow to affect the results of a determination.

I-2 REAGENTS

The reagents used shall be of a recognized analytical reagent quality.

I-2.1 Ethanol, absolute.

I-2.2 Internal standard, n-dodecanol or digol (diethylene glycol)

I-2.3 Calibration standard, propane - 1:3 - diol.

I-3 APPARATUS

I-3.1 Gas chromatographic apparatus having the required degree of accuracy. A stationary phase consisting of a mixture, by weight, of 25 per cent polyester* and 75 per cent diatomaceous earth is recommended.

I-3.2 Micro-pipette or micro-syringe or drawn out glass capillary tube.

I-4 PROCEDURE

It is not practicable to provide complete details of operating procedure for all the types of instrument which might be used, but the following generalization may be made:

Stationary phase: Purge the mixture of polyester and diatomaceous earth for 24 hours in a stream of nitrogen at 200°C before use.

Column: 1 - 2 mm diameter and as short as possible, depending on the apparatus used (columns 250 - 300 mm long have been used with success with flame ionization apparatus).

---

* **e. g. Poly - (ethylene glycol adipate), is suitable.**

Column temperature: 120 – 150°C.

Internal standard – With the preferred 250 – 300 mm packed column an internal standard is optional (though preferred). Since the glycerol is eluted in a short time, the propane - 1:3 - diol content may be determined directly by reference to the glycerol.

If longer columns are used an internal standard is necessary. Pure do-decanol or digol (diethylene glycol) is suitable.

When an internal standard is used, add to the glycerol an accurately weighed quantity of the standard, sufficient to give a concentration approximately equal to the expected concentration of propane 1 : 3 - diol. Carry out a preliminary series of experiments to determine the relation between the response factors for propane 1 : 3 - diol and the internal standard under the proposed sample test conditions.

Sample introduction on packed column - The preferred method is to add the sample directly by the drawn-out capillary, micro-pipette or micro-syringe. An equal volume of ethanol may be added as dilutant, to reduce the viscosity (after inclusion of any internal standard), but the ethanol trace may overlap the propane 1 : 3 - diol trace, in which case the ethanol should not used.

APPENDIX J

DETECTION OF SUGARS

J - 1 PRINCIPLE

The glycerol is heated with a reagent solution for 15 minutes on the steam bath. Development of a marked colour (usually brown) indicates the presence of a sugar.

J - 2 REAGENT

The reagent used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

Reagent solution – Dissolve 4 g of urea and 0.2 g of stannous chloride by heating with 10 ml of approximately 40 per cent (v/v)

sulphuric acid. (It is usually convenient to make at least 30 ml of solution).

J - 3 PROCEDURE

To each of two test tubes 150 mm (6 in) by 12.5 mm (5 in) add 4 drops of the glycerol under test. To one tube add 1 ml of the reagent solution and to the other add 1 ml of distilled water, as a control (Note 2). Immerse both tubes in a steam bath and examine after 15 minutes (Note 3). If a marked colour develops in the tube containing the reagent, sugar is present.

Note 1: A marked colour shows the presence of 0.25 per cent or more sugar.

Note 2: If preferred, a standard mixture can be made up of several crude glycerols known to be sugar-free, and 1 ml of the reagent solution added to 4 drops of this standard crude glycerol, and the whole subjected to the above test as control.

Note 3: The time is chosen as sufficient to give a significant colour change even with low concentration of sugars, though in many cases 5 minutes would suffice.

APPENDIX K

PREPARATION AND STANDARDISATION OF 0.125 N SODIUM HYDROXIDE SOLUTION (CARBONATE-FREE)

K-1 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

K-1.1 Sodium hydroxide, pellets.

K-1.2 Potassium hydrogen phthalate, acidmetric standard quality and of certified purity, dry.

K-1.3 Phenolphthalein indicator, 0.5 per cent ethanolic solution, prepared as in Appendix C.

K-2 APPARATUS

K-2.1 Container, of borosilicate glass, 20 millilitre convenient capacity, fitted with a rubber bung.

K-2.2 Sintered glass funnel, of borosilicate glass, porosity 3, diameter approximately 60 mm.

K-2.3 Buchner filter flask of borosilicate glass, 2 millilitre capacity.

K-2.4 Burette, 50 ml.

K-3 PROCEDURE

Dissolve 900 g of the sodium hydroxide in 900 ml of water in a 2 millilitre flask or a stainless steel beaker.

> **Note:** Smaller quantities of sodium hydroxide and proportionately smaller apparatus may be used, provided that the solution is made of the same concentration.

Loosely stopper the flask (or cover the beaker) and allow it to stand for 2 - 3 days. Filter the solution under an atmosphere of nitrogen, through the sintered glass funnel or a hardened filter paper into the Buchner flask using suction. Store the filtrate in a borosilicate glass bottle or stone crock with a well fitting rubber stopper. Weigh accurately, in a stoppered weighing bottle, about 10g of the sodium hydroxide solution. Transfer quantitatively to a 1000 ml volumetric flask, make up to the mark with water and mix well. Weigh accurately about 1 g of the potassium hydrogen phthalate. Transfer quantitatively to a 500 ml conical flask with small portions of water, finally adding enough water to make a total of about 100 ml. Add 0.5 ml of the phenolphthalein indicator and titrate with the dilute hydroxide solution from a 50 ml burette, to the first permanent pink colour. From the titration and the weight of phthalate and strong sodium hydroxide solution calculate the approximate weight percentage of sodium hydroxide in the latter and hence the weight required to prepare 17 millilitre (or such other volume as may be required) of 0.125 N sodium hydroxide solution.

Weigh the calculated amount of concentrated sodium hydroxide solution (to the nearest 0.1 g), transfer to the container already containing approximately 1 millilitre less than the required volume of water and dilute with additional water to the required volume; stopper the container and mix the solution thoroughly over a period of two hours. Allow to stand overnight. Weigh approximately 10 g of the potassium hydrogen phthalate into a glass dish and dry the material for two hours in an electric oven maintained at 120° C. Cool the salt in a desiccator.

Weigh accurately three portions of the dried salt, each of approximately 1 g into separate 500 ml conical flasks. Add approximately 100 ml of water to each flask and swirl to dissolve the contents.

Fill the burette with the unstandardised sodium hydroxide solution. Fit the top of the burette with a soda-lime tube. Allow the burette to attain laboratory temperature and carefully adjust the meniscus of the sodium hydroxide solution to the zero mark. Titrate each sample of potassium hydrogen phthalate solution in an atmosphere of nitrogen as follows:

Add the theoretical quantity, less 2 ml of the sodium hydroxide solution. Add 0.5 ml of the indicator solution, shake the contents of the flask, and continue the titration until the first permanent pink colour is obtained. Read the burette to 0.01 ml.

K-4 CALCULATION

$$\text{Normality of the sodium hydroxide solution} = \frac{Pm}{20.423\,T}$$

where P = percentage purity of the standard potassium hydrogen phthalate,

m = mass in grammes, of standard potassium hydrogen phthalate taken,

and T = volume, in millilitre of sodium hydroxide solution used.

After applying the calibration correction, the triplicate results for normality should agree within 0.000 15. Calculate the average normality.

APPENDIX L

SPECIFICATION FOR SODIUM PERIODATE FOR GLYCEROL DETERMINATION

L-1 APPEARANCE

The material shall be a white crystalline powder.

L-2 SOLUBILITY

The material shall dissolve to give a clear colourless solution when 1 g is shaken with 10 ml of water at 20° C.

L-3 PURITY

The material shall contain not less than 98.0 per cent by mass of sodium periodate ($NaIO_4$), determined by the following method:

L-3.1 Principle - Potassium iodide is added to an aqueous solution of the sodium periodate buffered with sodium hydrogen carbonate and the liberated iodine is titrated with a standard solution of sodium arsenite.

L-3.2 Reagents - The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

(i) Potassium iodide

(ii) Sodium hydrogen carbonate

(iii) Sodium arsenite, 0.1N solution. Weigh 2.473 g of arsenous oxide in a 250 ml squat beaker, add 20 ml of 10 per cent sodium hydroxide solution and warm on the steam bath until solution is complete. Cool, transfer quantitatively to a 500 ml volumetric flask, neutralize to litmus paper with N hydrochloric acid, make up to the mark with water and mix well.

Warning: Do not measure solution containing arsenic by means of a pipette filled by suction with the mouth: use a burette or other dispensing device.

(iv) Starch indicator, 1 per cent aqueous solution.

L-3.3 Procedure - Weigh accurately 0.36 g of the sodium periodate into a 250 ml glass-stoppered conical flask, add 100 ml of water and swirl to dissolve. Add 7.5 g sodium hydrogen carbonate followed by 3 g of potassium iodide, stopper the flask and allow to stand for exactly 15 minutes. Titrate the solution to a pale straw colour with 0.1 N sodium arsenite solution, add 5 ml of starch indicator and complete the titration.

L - 3.4 Calculation

$$\text{Sodium periodate } NaIO_4\text{, percent by mass} = \frac{1.070\,T}{m}$$

where T = volume, in millilitres of 0.1 N sodium arsenite solution required,

and m = mass, in grammes, of sodium periodate taken.

APPENDIX M

METHOD 1. - DETERMINATION OF FREE CAUSTIC ALKALI

M-1 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

M-1.1 Barium chloride, neutral 10 per cent solution.

M-1.2 Hydrochloric or sulphuric acid, 0.1 N solution.

M-1.3 Phenolphthalein indicator, 0.5 per cent ethanolic solution, prepared as in Appendix C.

M-2 PROCEDURE

Weigh accurately about 20 g of the sample into a 100 ml volumetric flask, dilute with approximately 50 ml of carbon dioxide-free water, add an excess of the barium chloride solution, make up to

the mark and mix. Allow the precipitate to settle, draw off 50 ml of the clear liquid and titrate with the acid, using the phenolphthalein solution as indicator.

M-3 CALCULATION

$$\text{Free caustic alkali, per cent as } Na_2O = \frac{0.62\ T}{m}$$

where T = volume, in millilitres of 0.1N acid required,

and m = mass, in grammes, of sample taken.

METHOD 2. - DETERMINATION OF TOTAL ALKALINITY

M-4 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

M-4.1 Hydrochloric or sulphuric acid, 0.1N solution.

M-4.2 Methyl orange indicator, 0.1 per cent aqueous solution.

M-5 PROCEDURE

Dissolve the ash obtained by the procedure given in Appendix D in 50 ml of hot water, cool to room temperature and titrate with the acid, using the methyl orange solution as indicator.

M-6 CALCULATION

$$\text{Total alkalinity per cent, as } Na_2O = \frac{0.31\ T}{m}$$

where T = volume, in millilitre of 0.1 m acid required,

and where m = mass, in grammes, of sample taken for ash.

METHOD 3. - DETERMINATION OF CARBONATE ALKALINITY

M-7 REAGENTS

The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

M-7.1 Hydrochloric or sulphuric acid, 0.1 N solution.

M-7.2 Sodium hydroxide, carbonate-free, 0.1 N solution.

M-7.3 Phenolphthalein indicator, 0.5 per cent ethanolic solution, prepared as in Appendix C.

M-8 PROCEDURE

Weigh accurately about 10 g of the sample, dilute with 50 ml of water, and add sufficient of the acid to neutralize the total alkalinity found in Test 2, plus an excess of 1.0 ml. Boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with carbon dioxide-free water, cool rapidly and titrate the excess acid with the sodium hydroxide solution using phenolphthalein as indicator.

M-9 CALCULATION

Free caustic and carbonate alkalinity per cent, as Na_2O

$$= \frac{0.31\ (V - T)}{m}$$

where V = volume, in millilitres of 0.1N acid added,

T = volume, in millilitres of 0.1N sodium hydroxide required,

and m = mass, in grammes, of sample taken.

Carbonate alkalinity, as $Na_2O = (A_2 - A_1)$ per cent

where A_2 = free caustic and carbonate alkalinity,

and A_1 = free caustic alkalinity, as determined in Method 1.

APPENDIX N

DETERMINATION OF SPECIFIC GRAVITY

Note: It is advisable that all tests should be carried out in duplicate.

N-1 DEFINITION

For the purposes of this Appendix, the following definition applies. The specific gravity at 15.5/15.5° C in air of glycerol is the ratio of the weight in air of a given volume of the glycerol at 15.5° C to that of the same volume of water at that temperature, the weighing being made with weights adjusted to balance brass weights in air.

The above definitions of specific gravity* differs from other definitions of the same property in use in other fields; for example, the definitions given in B. S. 718‡ is different and the definitions in use in the petroleum industry are also different. The definition is, however, widely used for glycerol and has been chosen because glycerol is commonly sold by its apparent weight in air and not by its mass; a simple factor is thus provided for the conversion of volumes to weight.

N - 2 APPARATUS

N - 2.1 Density bottle, capacity not less than 25 ml

or

N - 2.2 Pycnometer of similar capacity.

N - 3 PROCEDURE

Calibrate the specific gravity bottle or pycnometer as follows:

Weigh the clean dry bottle or pycnometer, then fill it with cooled distilled water at about 10° C and maintain it in a bath of water at 15.5° C until it reaches that temperature. If a bottle is used, insert the stopper in such a way that the capillary is completely filled with water, and then maintain the filled bottle at 15.5° C until no further alteration in volume occurs. Wipe the stopper. If a pycnometer is used, adjust the volume of liquid to the fixed mark. Remove the bottle or pyknometer from the bath, dry the outside, allow to stand in a tared dish for a short time and weigh.

---

* The term adopted by the International Organization for Standardization for this concept is 'relative density with reference to water'. The ISO definition, however, is equivalent to the ratio of the true masses and not to the ratio of the weights in air.

‡ B. S. 718 - 'Density hydrometers and specific gravity hydrometers.'

APPENDIX O

GLYCEROL CONTENT, SPECIFIC GRAVITY AT 15.5/15.5°C AND APPARENT DENSITY AT 20°C OF AQUEOUS SOLUTIONS OF PURE GLYCEROL

Glycerol per cent	Specific gravity at 15.5/15.5° C		Apparent density at 20° C g/ml	Glycerol per cent	Specific gravity at 15.5/15.5° C		Apparent density at 20°C g/ml
	Apparent	True*			Apparent	True*	
100	1.265 32	1.265 01	1.260 1				
99	1.262 75	1.262 75	1.257 6	73	1.193 40		1.186 6
98	1.260 20	1.259 85	1.255 0	72	1.190 70		1.185 8
97	1.257 60	1.257 30	1.252 4	71	1.187 95		1.183 1
96	1.255 00	1.254 70	1.249 8	70	1.185 20	1.184 95	1.180 3
95	1.252 45	1.252 15	1.247 3	69	1.182 40		1.177 6
				68	1.179 65		1.174 8
94	1.249 80	1.249 50	1.244 7				
93	1.247 15	1.246 85	1.242 1	67	1.176 85		1.172 0
92	1.244 50	1.244 20	1.239 4	66	1.174 10		1.169 3
				65	1.171 30	1.171 10	1.166 6
91	1.241 85	1.241 55	1.236 8				
90	1.239 20	1.238 95	1.234 1	64	1.168 55		1.163 8
89	1.236 55	1.236 25	1.231 5	63	1.165 75		1.161 2
				62	1.163 00		1.158 3
88	1.233 90	1.233 60	1.228 8				
87	1.231 20	1.230 95	1.226 1	61	1.160 20		1.155 5
86	1.228 55	1.228 30	1.223 5	60	1.157 45	1.157 25	1·152 8
				59	1.154 65		1.150 1
85	1.225 90	1.225 65	1.220 8				
84	1.223 25	1.223 00	1.218 1	58	1.151 90		1.147 3
83	1.220 55	1.220 30	1.215 5	57	1.149 10		1.144 6
				56	1.146 35		1.141 9
82	1.217 90	1.217 65	1.212 8				
81	1.215 25	1.215 00	1.210 1	55	1.143 55	1.143 40	1.139 1
80	1.212 60	1.212 35	1.207 5	54	1.140 80		1.136 4
				53	1.138 00		1.133 6
79	1.209 85		1.204 7				
78	1.207 10		1.202 1	52	1.135 25		1.130 8
77	1.204 40		1.199 4	51	1.132 45		1.128 1
				50	1.129 70	1.129 55	1.125 4
76	1.201 65		1.196 6				
75	1.198 90	1.198 65	1.193 9				
74	1.196 15		1.191 2				

NOTE: The table was extracted from those complied by Bosart and Snoddy, published in 'Industrial and Engineering Chemistry', April 1927.
*Reduced to vacuum.

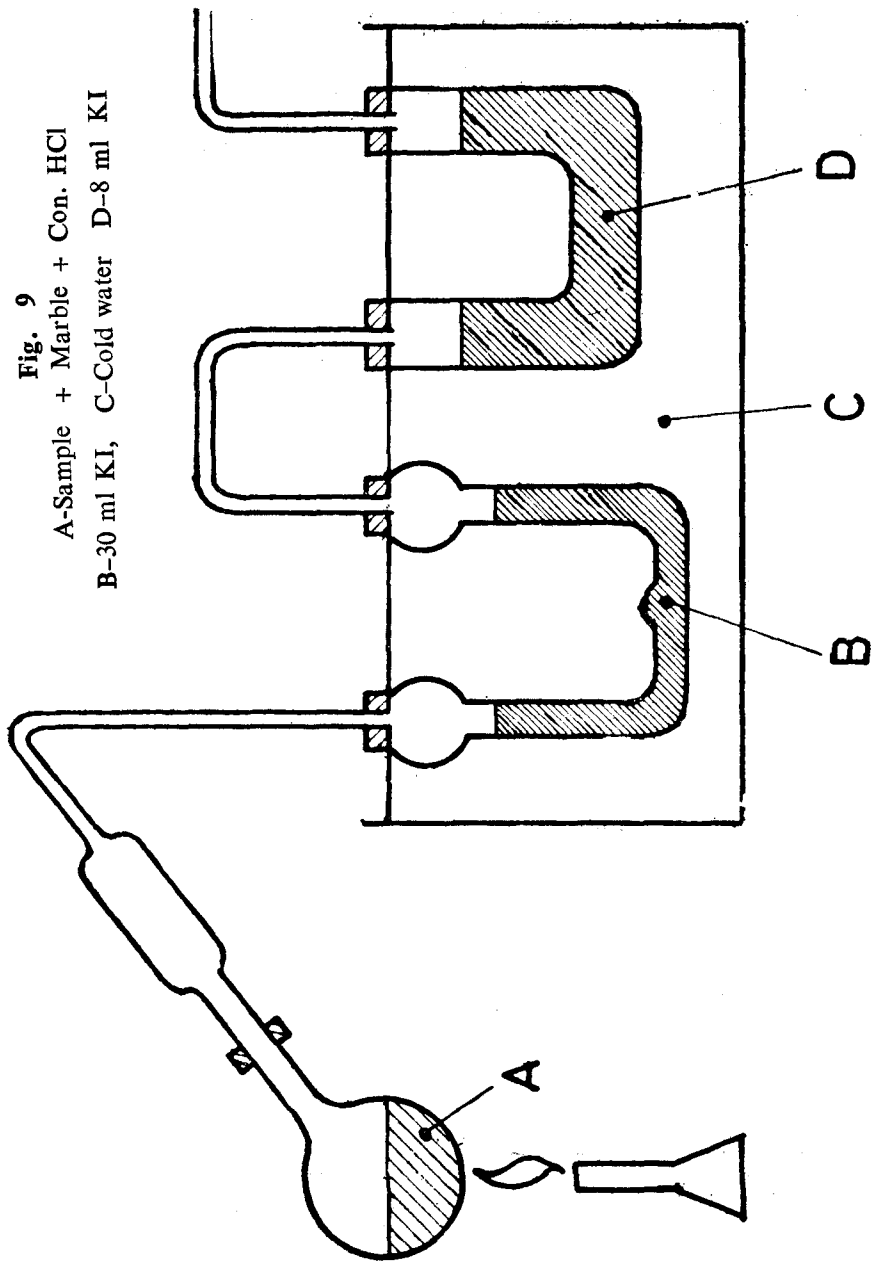

Fig. 9
A-Sample + Marble + Con. HCl
B–30 ml KI, C–Cold water D–8 ml KI

Empty and dry the bottle or pycnometer. Fill it with the sample previously cooled to about 5 deg. C below the temperature of 15.5°C, making sure no air bubbles are present. Maintain the bottle or pycnometer in a bath adjusted to 15.5°C until it has reached that temperature. If a bottle is used, insert the stopper in such a way that the capillary is completely filled with glycerol and then maintain at 15.5°C until no further alteration in volume occurs. Wipe the stopper. If a pycnometer is used, adjust the volume to the fixed mark. Remove the apparatus from the bath, dry the outside, allow to stand for a short time in the tared dish and weigh. Make all weighings in air with weights adjusted to balance brass weights in air.

N-4 CALCULATION

$$\text{Specific gravity of the glycerol at } 15.5/15.5^\circ \text{ C in air} = \frac{m_1}{m_2}$$

where m_1 = mass, in grammes, of glycerol obtained in the test,

and m_2 = mass, in grammes, of water obtained in the calibration test.

APPENDIX P

METHOD FOR ESTIMATION OF CHLORATE IN CRUDE GLYCERINE

P-1 PRINCIPLE

Chlorate evolve chlorine upon treatment with concentrated hydrochloric acid and may be determined with accuracy by passing the chlorine evolved into excess of potassium iodide solution and titrating the liberated iodine with standard sodium thiosulphate solution.

P-2 THEORY

$$KClO_3 + 6HCl \longrightarrow KCl + 3Cl_2 + 3H_2O$$

$$3Cl_2 + 6KI \longrightarrow 6KCl + 3I_2$$

$$6Na_2S_2O_3 + 3I_2 \longrightarrow 6NaI + 3Na_2S_4O_6$$

$$Na_2S_2O_3 \equiv I \equiv \frac{KClO_3}{6}$$

1ml 0.2N $Na_2S_2O_3 \equiv 0.00278$ g. $ClO_3 \equiv 0.00409$g. $KClO_3$

P-3 REAGENTS

P-3.1 Potassium Iodide solution - dissolve 2.5g of potassium iodide solution in 42ml of distilled water.

P-3.2 Concentrated hydrochloric acid.

P-3.3 Piece of marble, 5-10g - used to obtain a steady stream of carbon dioxide.

P-3.4 Standard sodium thiosulphate solution - 0.2N.

P-3.5 1% solution of starch - used as indicator near the end point.

P-4 APPARATUS

P-4.1 100ml round bottom quickfit flask.

P-4.2 Two U-tubes connected as shown in Figure 9 and immersed in a bath of cold water.

P-4.3 Quickfit delivery tube.

P-5 PROCEDURE

Weigh accurately approximately 1g. of crude glycerine into the quickfit and to this add a small piece of marble. Introduce 34 ml of the potassium iodide solution into the first U-tube and 8 ml into the second U-tube and connect the two together. Add 20 ml of concentrated hydrochloric acid to the content of the flask and connect it by means of the delivery tube to the first U-tube. Heat the mixture very gently so that the chlorine is slowly evolved. Increase the temperature gradually to the boiling point, the carbon dioxide evolved expels all the chlorine, and this liberates the iodine from the potassium iodide solution. Immediately before the heating is stopped, disconnect the U-tubes from the delivery tube in order to prevent the solution in the absorption vessels from passing back into the flask. Transfer the contents of both U-tubes to a conical flask and titrate the liberated iodine at once with standard 0.2N sodium thiosulphate until the solution has a pale yellow colour. Add 2ml of starch solution and continue the addition of the thiosulphate solution slowly until the solution is just colourless.

SLS CERTIFICATION MARK

The Sri Lanka Standards Institution is the owner of the registered certification mark shown below. Beneath the mark, the number of the Sri Lanka Standard relevant to the product is indicated. This mark may be used only by those who have obtained permits under the SLS certification marks scheme. The presence of this mark on or in relation to a product conveys the assurance that they have been produced to comply with the requirements of the relevant Sri Lanka Standard under a well designed system of quality control inspection and testing operated by the manufacturer and supervised by the SLSI *which includes surveillance inspection of the factory, testing of both factory and market samples.*

Further particulars of the terms and conditions of the permit may be obtained from the Sri *Lanka Standards Institution, 17, Victoria Place, Elvitigala Mawatha, Colombo 08.*

Printed at SLSI (Printing Unit)

SRI LANKA STANDARDS INSTITUTION

The Sri Lanka Standards Institution (SLSI) is the National Standards Organization of Sri Lanka established under the Sri Lanka Standards Institution Act No. 6 of 1984 which repealed and replaced the Bureau of Ceylon Standards Act No. 38 of 1964. The Institution functions under the Ministry of Science & Technology.

The principal objects of the Institution as set out in the Act are to prepare standards and promote their adoption, to provide facilities for examination and testing of products, to operate a Certification Marks Scheme, to certify the quality of products meant for local consumption or exports and to promote standardization and quality control by educational, consultancy and research activity.

The Institution is financed by Government grants, and by the income from the sale of its publications and other services offered for Industry and Business Sector. Financial and administrative control is vested in a Council appointed in accordance with the provisions of the Act.

The development and formulation of National Standards is carried out by Technical Experts and representatives of other interest groups, assisted by the permanent officers of the Institution. These Technical Committees are appointed under the purview of the Sectoral Committees which in turn are appointed by the Council. The Sectoral Committees give the final Technical approval for the Draft National Standards prior to the approval by the Council of the SLSI.

All members of the Technical and Sectoral Committees render their services in an honorary capacity. In this process the Institution endeavours to ensure adequate representation of all view points.

In the International field the Institution represents Sri Lanka in the International Organization for Standardization (ISO), and participates in such fields of standardization as are of special interest to Sri Lanka.

Printed at the Sri Lanka Standards Institution, 17, Victoria Place, Elvitigala Mawatha, Colombo 08.