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METHODS FOR THE DETERMINATION OF ARSENIC

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BUREAU OF CEYLON STANDARDS

METHODS FOR THE DETERMINATION OF ARSENIC

S.L.S. 312 : 1976

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BUREAU OF CEYLON STANDARDS
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COLOMBO-3.

SRI LANKA STANDARD METHODS FOR THE DETERMINATION OF ARSENIC

FOREWORD

This Sri Lanka Standard was prepared by the Drafting Committee of the Bureau on Chemical Test Methods. It was approved by the Agricultural & Chemicals Divisional Committee of the Bureau of Ceylon Standards and was authorised for adoption and publication by the Council of the Bureau on 4th February, 1976.

The following publications have been consulted in the preparation of this standard:

(i) *British Standards Institution*—Methods for the determination of arsenic (Silver diethyl dithio carbamate procedure) (B.S. 4404-1968)

(ii) *Garratt, D. C.*—Quantitative analysis of drugs 1964 erd ed. Chapman & Hall, London.

(iii) *General Medical Council*—British Pharmacopocia 1968 — Pharmaceutical Press London.

(iv) *Analytical Methods Committee*—The determination of small amounts of Arsenic in organic matter Analyst vol. 85, 1960.

1. SCOPE

This standard prescribes methods for the determination of arsenic.

2. METHODS

The modified Gutzeit method of test for arsenic shall be employed in cases where the arsenic content is not needed and only a limit is desired.

In cases where the actual arsenic content is to be determined, the silver diethyl dithiocarbamate method shall be followed. The method is suitable for quantities of arsenic (as As) ranging from 1μg to 1000μg in the aliquot used for the assay.

2.1 Modified Gutzeit Method

2.1.1 Apparatus—(*see Fig.* 1)—A wide mouthed bottle capable of holding 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). It is drawn out at one end to a diameter

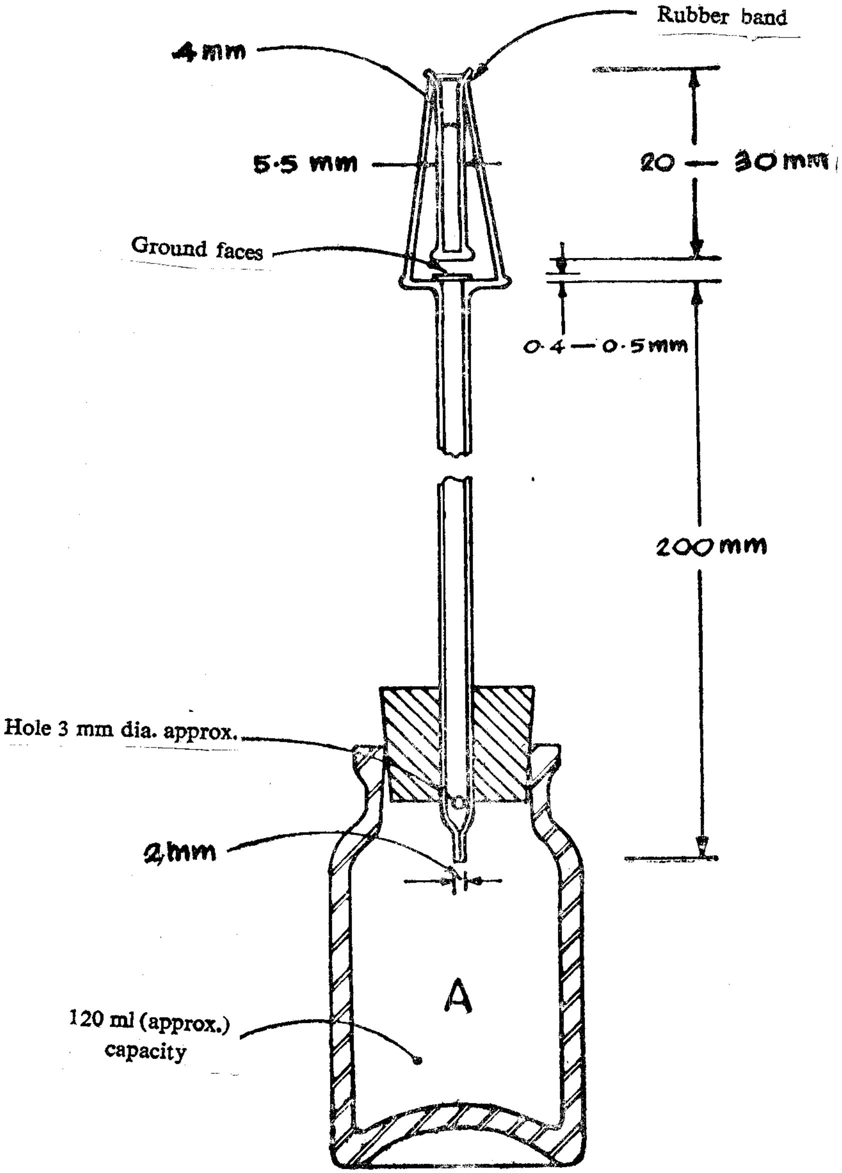

Fig. 1– Apparatus for Gutzeit Method

of about 1 mm and a hole not less than 2 mm in diameter is blown in the side of the tube, near the constricted part. 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 slightly rounded or ground smooth.

Two rubber bungs (about 25 × 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 contrivances satisfying the conditions described under the general test.

2.1.2 Reagents & Materials

(i) *Arsenic Solution Dilute AsT*

Strong arsenic solution AsT	1 ml
Water, sufficient to produce	100 ml

Dilute arsenic solution, AsT must be freshly prepared; 1 ml contains 0.01 mg of arsenic, As.

(ii) *Arsenic Solution Strong AsT*

Arsenic trioxide	0.132 g
Hydrochloric acid	50 ml
Water, sufficient to produce	100 ml

(iii) *Bromine Solution AsT*

Bromine	30 g
Potassium bromide	30 g
Water, sufficient to produce	100 ml

It Complies with the following Test:

Evaporate 10 ml on a water bath nearly to dryness, add 59 ml of water, 10 ml hydrochloric acid AsT and sufficient stannous chloride solution AsT to reduce the remaining bromine, and apply the general test; the stain produced is not deeper than a 1 ml standard stain, showing that the proportion of arsenic present does not exceed 1 mg/kg.

(iv) *Hydrochloric Acid AsT*—Hydrochloric acid which complies with the following additional tests:

(*a*) Dilute 10 ml with sufficient water to produce 50 ml, add 5 ml of ammonium thiocyanate solution and stir immediately; no colour is produced.

(*b*) To 50 ml add 0.2 ml of bromine solution AsT, evaporate on a water bath until reduced to 16 ml, adding more bromine solution AsT if necessary, in order that an excess, as indicated by the colour may be present throughout the evaporation; add 50 ml of water and 5 drops of stannous chloride solution AsT, and apply the general test; the stain produced is not deeper than a 0.2 ml standard stain prepared with the same acid, showing that the portion of arsenic present does not exceed 0.05 mg/kg.

(v) *Mercuric Chloride Paper*—Smooth white filter paper, not less than 25 mm in width, soaked in a saturated solution of mercuric chloride, pressed to remove superfluous solution, and dried at about 60°C in the dark. The grade of the filter paper shall be such that the mass in g per sq. m shall be between 65 and 120; the thickness in mm of 400 papers shall be approximately equal, numerically, to the mass in g per sq. m.

Note: Mercuric chloride paper should be stored in a stoppered bottle in the dark. Paper which has been exposed to sunlight or to the vapour of ammonia affords a lighter coloured stain or no stain at all when employed in the quantitative test for arsenic.

(vi) *Lead Acetate Solution*, $10\% \frac{m}{V}$

Add sufficient acetic acid to obtain a clean solution.

(vii) *Lead Acetate Paper* (*dry*)—Soak filter paper strips of 70 × 50 mm size in lead acetate solution. Take out strips before use and dry in an atmosphere free from hydrogen sulphide.

(viii) *Potassium Iodide AsT*—Potassium iodide which complies with the following additional test:— Dissolve 10 g in 25 ml of hydrochloric acid AsT and 35 ml of water, add 2 drops of stannous chloride solution AsT and apply the general test: no visible stain is produced.

(ix) *Stannous Chloride Solution AsT*—Prepare from stannous chloride solution by adding an equal volume of hydrochloric acid, boiling down to the original volume, and filtering through a fine grained filter paper.

It Complies with the following Test:

To 10 ml add 6 ml of water and 10 ml of hydrochloric acid AsT, distil and collect 16 ml. To the distillate add 50 ml of water and 2 drops of stannous chloride solution AsT, and apply the general test—the stain produced is not deeper than a 1 ml standard stain, showing that the proportion of arsenic present does not exceed 1 mg/kg.

(x) *Standard Hydrochloric Acid AsT*

Stannous chloride solution AsT	1 ml
Hydrochloric acid AsT	100 ml

(xi) *Zinc AsT*—Granulated zinc which complies with the following additional test:

Add 10 ml of stannated hydrochloric acid AsT to 50 ml of water, and apply the general test, using 10 g of the zinc, but allowing the action to continue for one hour; no visible stain is produced (limit of arsenic). Repeat the test with the addition of 0.1 ml of dilute arsenic solution AsT; a faint but distinct yellow stain is produced (test for sensitivity).

2.1.3 **Procedure**—By a method of procedure, suitable to the particular needs of each substance*, † there is prepared from the substance to be tested a solution which may or not contain that substance, but contains the whole of the arsenic (if any) originally present in that substance. This solution, referred to as 'the solution to be examined', is used in the actual test.

General Test—The glass tube is lightly packed with either cotton wool, previously moistened with lead acetate solution and dried or with dry lead acetate paper so that the upper surface of the cotton wool is not less than 25 mm below the top of the tube. The upper end of the tube is then inserted into the narrow end of one of the pair of rubber bungs, either to a depth of about 10 mm when the tube has a rounded off end, or so that the ground end

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* Refer S.L.S. 242 : "Methods for the destruction of Organic Matter.

† In the presence of excessive heavy metals, the distillation procedure given in Appendix B shall be used.

of the tube is flush with the larger end of the bung. A piece of mercuric chloride paper is placed flat on the top of the bung, and the other bung placed over it and secured by means of the rubber band or spring clip, in such a manner that the borings of the two bungs (or the upper bung and the glass tube) meet to form a true tube of 6.5 mm diameter interrupted by a diaphragm of mercuric chloride paper.

Instead of this method of attaching the mercuric chloride paper any other method may be used provided (1) that the whole of the evolved gas passes through the paper; (2) that the portion of the paper in contact with the gas is a circle of 6.5 mm diameter; and (3) that the paper is protected from sunlight during the test.

The solution to be examined, prepared as specified above, is placed in the wide mouthed bottle, 1 g of potassium iodide AsT and 10 g of zinc AsT are added and the prepared glass tube is placed quickly in position. The action is allowed to proceed for forty minutes. The yellow stain which is produced on the mercuric chloride paper if arsenic is present is compared by daylight with the standard stains produced by operating in a similar manner with known quantities of dilute arsenic solution AsT. The comparison of the stains is made immediately at the completion of the test. The standard stains used for comparison are freshly prepared; they fade on keeping.

By matching the depth of colour with standard stains, the proportion of arsenic in the substance may be determined. A stain equivalent to the 1 ml standard stain produced by operating on 10 g of a substance indicates that the proportion of arsenic is 1 mg/kg.

Note: 1. The action may be accelerated by placing the apparatus on a warm surface care being taken that the mercuric chloride paper remains quite dry throughout the test.

2. The most suitable temperature for carrying out the test is generally about 40°C, but because the rate of evolution of the gas varies somewhat with different batches of zinc AsT, the temperature may be adjusted to obtain a regular, but not violent, evolution of gas.

3. The tube must be washed with hydrochloric acid AsT, rinsed with water, & dried between successive tests.

Standard Stains—Solutions are prepared by adding 50 ml of water, 10 ml of stannated hydrochloric acid AsT and quantities of dilute arsenic solution AsT varying from 0.2 ml to 1 ml. The resulting solutions, when treated as described in the general test, yield stains on the mercuric chloride paper referred to as the standard stains.

2.2 Silver Diethyldithiocarbamate Method

2.2.1 Interferences—Under the test conditions antimony and germanium are reduced to hydrides which give colorations with the solution of silver diethyldithiocarbamate in pyridine.

Salts of chromium, cobalt, copper, mercury, molybdenum, nickel, palladium and silver may interfere with the quantitative evolution and/or absorption of arsine, as may antimony and germanium in amounts larger than those associated with colour enhancement.

When applying this determination to any particular product consideration should be given to the likely effect of such interferences.

Note: The peak in the absorption curve due to the reaction of stibine is at about 515 nm. It has been shown that when measurements are made at 540 nm, amounts of antimony below 100μg show a positive error equivalent of up to 4% of the mass of antimony present. Under similar conditions the positive interferences of germanium is insignificant.

Further it has been shown that quantitative recoveries of arsenic are obtained even when the test solution contains the following :—

Upto	50 mg	copper or silver;
Upto	5 mg	cobalt or nickel;
Upto	1 mg	chromium or mercury;

Upto 0.05 mg concentrated nitric acid, 70% $\frac{m}{m}$.

2.2.2 Apparatus—The following apparatus is required:

(i) Evolution and absorption apparatus, of a form to ensure complete absorption of arsine. Suitable forms of apparatus are shown in Figs. 2 & 3.

1. Conical flask 100 ml for the evolution of arsine (A);
2. Connecting tube to trap hydrogen sulphide (B);
3. Absorption tube (C);
4. A spring clip to ensure the spherical joint connecting B & C.

(ii) *Spectrophotometer with* 10 *mm Cells*

Note 1 : If only a filter type instrument is available it has been found that an Ilford No. 605 or equivalent filter is suitable. It should be appreciated that because of the wide spectral band measured, interferences may be very much more significant.

Note 2 : All new glass flasks used in the determination of arsenic should be washed with hot concentrated sulphuric acid ($d = 1.84$) (CAUTION) rinsed thoroughly with distilled water and well drained. It is advisable that all flasks that have been used with samples of high arsenic content be cleaned after use in a similar manner.

Note 3 : It is inadvisable to rinse the flasks with organic solvents, some of which have been shown to have an adverse effect on the evolution of arsine.

The rest of the apparatus may be cleaned with organic solvents and thoroughly dried.

2.2.3 Reagents and Materials—*General*—All reagents used shall be of a recognised AsT quality. Water used shall be glass distilled water.

(i) Either (1) Hydrochloric acid*, concentrated, 36% $\left(\frac{m}{m}\right)$ (11 N) or (2) Sulphuric acid, concentrated, 98% $\left(\frac{m}{m}\right)$ (36 N).

(ii) Potassium iodide, 15 g/100 ml solution. This solution should be freshly prepared.

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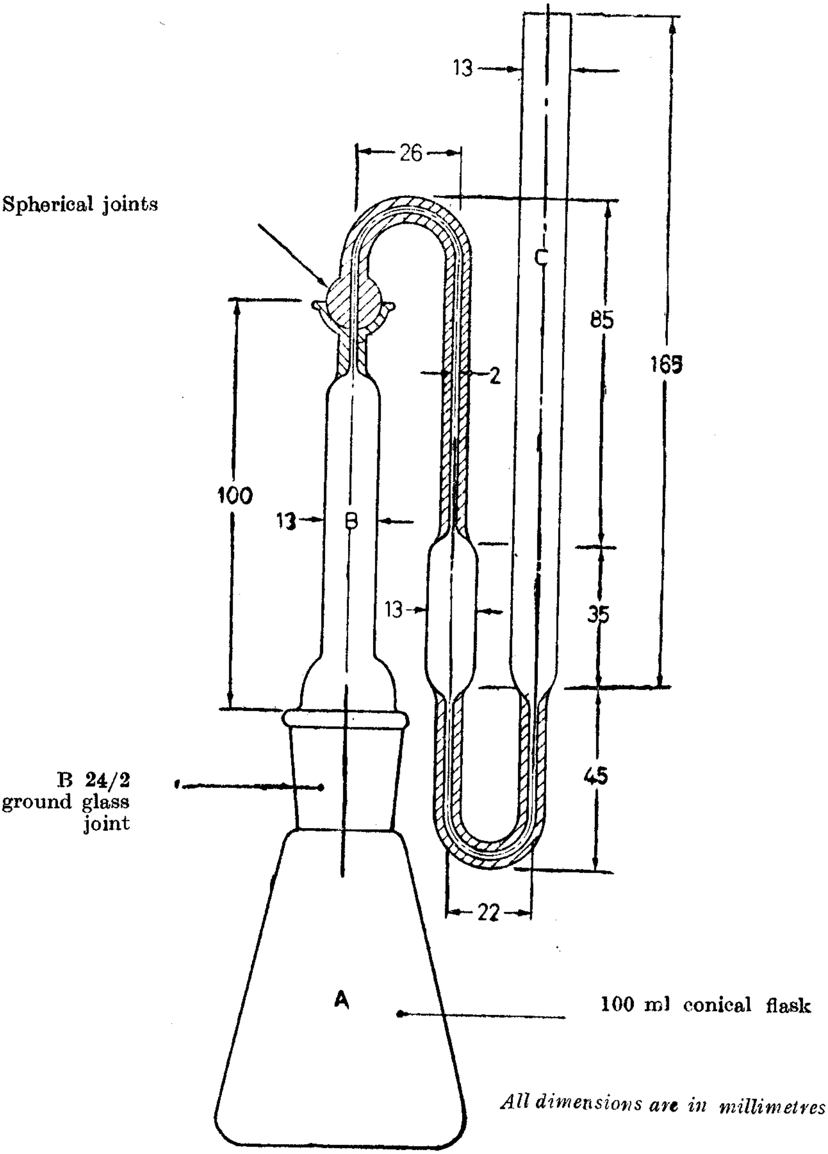
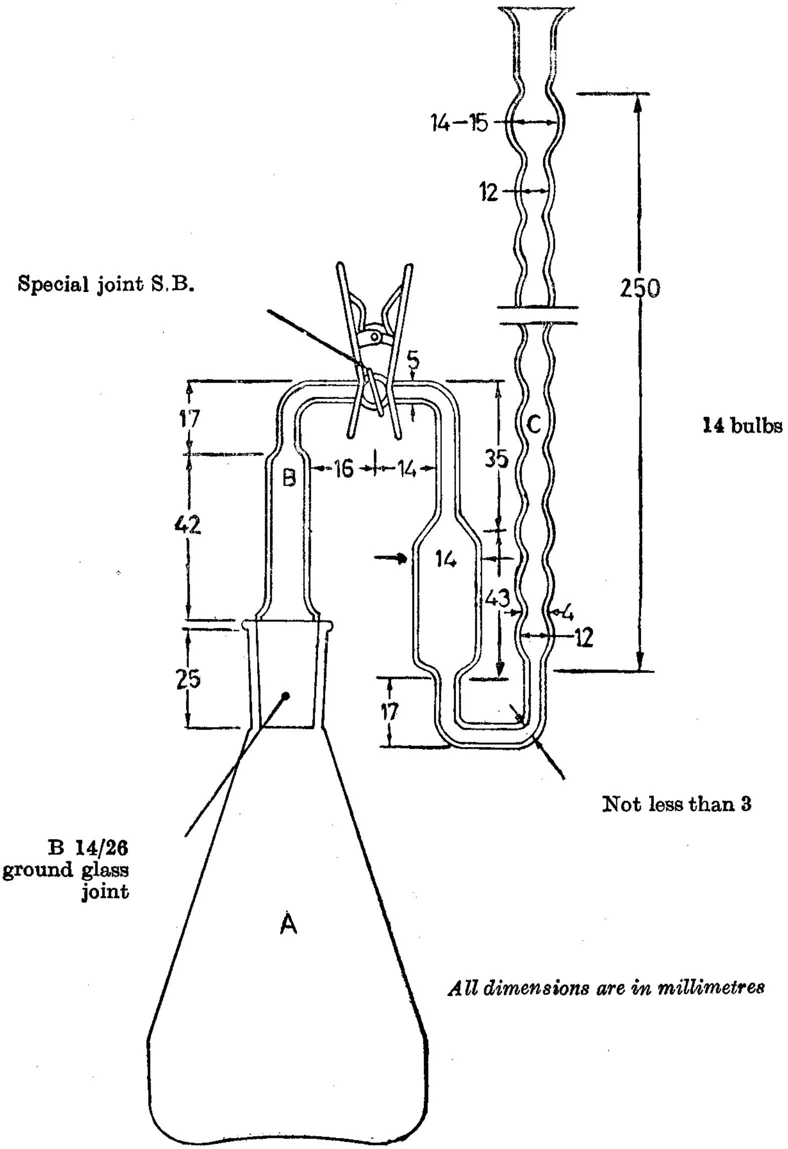
* Some supplies of hydrochloric acid and zinc do not to give quantitative yields of arsine; such supplies should be discarded.



All dimensions are in millimetres

Fig. 2 – Apparatus for the diethyldithiocarbamate method



All dimensions are in millimetres

Fig. 3 - Alternative form of apparatus

(iii) *Stannous Chloride Solution*—Dissolve 40 g of stannous chloride dihydrate in a mixture of 25 ml of water and 75 ml of concentrated hydrochloric acid, d = 1.18. Discard this solution if an appreciable deposit forms.

(iv) *Silver Diethyldithiocarbamate*—5 g/l solution in water white pyridine. Dissolve 1 g of silver diethyldithiocarbamate* in water white pyridine, (d = 0.980 approx.) and dilute to 200 ml with this pyridine. Store in a well stoppered glass bottle protected from light. This solution is stable for about 2 months.

Using good quality commercial silver diethyldithiocarbamate or that prepared as in Appendix A the absorption using 5 ml in 10 ml cells will be of the order of 0.04 per microgramme of arsenic.

(v) *Standard Arsenic Solutions*

(*a*) Stock arsenic solution, 0.1 g/l. Dissolve 0.132 g of dried arsenic trioxide in 20 ml of 350 g/l sodium hydroxide solution. Dilute with about 100 ml of water, add slowly 10 ml of concentrated sulphuric acid (d=1.84) and dilute with water to 1000 ml.

(*b*) Standard arsenic solution, 1 μg/ml, immediately before use dilute 10 ml of the stock arsenic solution to 1000 ml with water.

(*c*) Zinc†, granular or shot, 0.5 mm to 1.0 mm (16 mesh to 30 mesh).

(vi) *Absorbent Cotton Wool Impregnated with Lead Acetate*—Dissolve 50 g of lead acetate trihydrate in 250 ml of water. Saturate wool with this solution, drain, tightly press and dry under vacuum at room temperature.

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* Silver diethyldithiocarbamate of suitable reagent quality is available commercially. It may also be prepared from sodium diethyldithiocarbamate by the method described in Appendix A.

† Some supplies of hydrochloric acid and zinc have been found not to give quantitative yields of arsine; such supplies should be discarded.

2.2.4 Procedure

Note: Because of the noxious nature of pyridine the evolution stage should be performed under a fume hood.

Preparation of a Calibration Curve—The calibration curve shall be confirmed every time a new solution of the silver diethyldithiocarbamate reagent is prepared.

Arsine Evolution—Into a series of 100 ml conical flasks transfer aliquots of the standard arsenic solution corresponding to 0, 2, 4, 6, 8 and 10 μg of arsenic and treat each in the following manner.

Add 10 ml of the concentrated hydrochloric acid and dilute to 45 ml to 55 ml with water. Add 2.0 ml of the potassium iodide solution and 2.0 ml of the stannous chloride solution. Mix and allow to stand for 15 minutes to 20 minutes.

Lightly pack the top third of the connecting tube with the impregnated cotton wool and assemble the absorption train. Transfer to the absorption tube 5.0 ml of silver diethyldithiocarbamate solution.

After the standing period introduce 5 g of the zinc into the conical flask and rapidly reassemble the apparatus.

Allow the reaction to continue for 45 to 60 minutes at room temperature.

Spectrophotometric Measurements—Disconnect the absorption tube and tilt the absorber so that the reagent solution flows back and forthe between the absorber and bulb to dissolve any red solid and to mix the solution thoroughly. Transfer the solution to the photometric cell and measure its absorbance at the wavelength of maximum absorption (540 nm) using water in the comparison cell.

Note: The colour of the solution is stable for several hours but because of the small volume it is necessary to take special care to prevent concentration of the solution by evaporation of solvent.

Plotting—For each solution calculate a corrected absorbance by subtracting the reading obtained for the solution containing no standard arsenic solution from the observed reading. Draw a graph plotting the corrected absorbance of the solutions against their arsenic contents.

2.2.5 **Determination**—*Test Sample and Preparation of Test Solution*—Follow the instructions given in C.S. *†. These instructions shall give the appropriate mass of sample and result in the preparation of a final test solution 45 ml to 55 ml in volume containing $1 \mu g$ to $10 \mu g$ of arsenic and approximately 2.5 N with regard to hydrochloric or sulphuric acid.

Test—Transfer the test solution to the conical flask, cool to room temperature if necessary, and proceed following the instructions given in Clause 2.2.4.

Blank Test—Carry out a blank test, following the instructions given in Clause 2.2.5 omitting the sample.

Note: For some materials it may be necessary for special instructions to be given regarding the procedure for preparation of the blank test solution.

2.2.6 **Calculation**—Calculate a corrected absorbance by subtracting the value obtained for the blank solution from that obtained for the test solution and read from the calibration curve the corresponding mass of arsenic.

$$\text{Arsenic content, mg/kg by mass} = \frac{M_1}{M_2},$$

where, M_1 = mass, in microgrammes, of arsenic found
and M_2 = mass, in grammes, of sample in the solution tested.

2.3 **Atomic Absorption Spectrophotometric Method**—The atomic absorption spectrophotometric method is to be adopted if and when it could be used as a routine method in Sri Lanka.

APPENDIX A

PREPARATION OF PURIFIED SILVER DIETHYLDITHIOCARBAMATE

A-1 **Purification of Sodium Diethyldithiocarbamate**—Dissolve 10 g of sodium diethyldithiocarbamate $(C_2H_5)_2NCS.SNa.3H_2O$ in 35 ml of ethanol $\left(95\% \frac{V}{V}\right)$ and filter. Add to this solution, with continuous stirring, 100 ml of diethyl ether. Filter with suction, wash the precipitate with ether and dry in air.

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* Refer S.L.S. 242 — "Methods for the destruction of Organic Matter".

† In the presence of excessive heavy methods, the distillation procedure given in Appendix B shall be used.

A-2 Preparation of the Reagent—Dissolve 2.2 g of purified sodium diethyldithiocarbamate in 100 ml water. Dissolve 1.7 g of silver nitrate in 100 ml water. Mix the two solutions slowly with continuous agitation. Keep the mixture at a temperature below 10°C. Decant the clear solution wash the precipitate three times with water, at a temperature below 10°C. Filter and dry the product in vacuum at room temperature. Preserve in a cool place protected from light.

APPENDIX B

ISOLATION OF ARSENIC BY DISTILLATION

This procedure is carried out on the test solution and the blank solution after the destruction of organic matter only if one of the following conditions is encountered:

(*a*) the total heavy metal content of the test solution exceeds 1000μg, or

(*b*) there is an excessive amount of antimony present in the test solution.

Note: In the distillation method, it is important to use the relative amounts of reagents as specified, as this ensures a steady evolution of hydrogen chloride gas throughout the distillation, which is essential to the success of the method Serious divergence from the recommended amounts is liable to lead either to too vigorous a reaction in the early stages of distillation, whereby arsenius chloride may be swept through the receiver or to the evolution of water, with the consequent failure to obtain quantitative entrainment of the arsenic.

Reagent—Chloride—Hydrazine—Bromide Mixture—ground together intimately a mixture 5 parts by mass sodium chloride,

0.5 parts by mass hydrazine sulphate and 0.02 parts by mass potassium bromide.

The following directions assume that 8 – 10 ml of sulphuric acid have been used in the wet decomposition; if less acid has been used, if should be supplemented at this point. If the wet decomposition has not been carried out in Kjeldahl flask of the distillation apparatus (see Fig. 4), transfer the solution to it, rinsing in with the minimum amount of water, evaporate to fuming and allow to cool.

To the cold residue in the flask add 7 ml of water and cool. Add 5 g of the chloride–hydrazine–bromide mixture, avoiding contamination of the ground portion of the neck of the flask and fit the condenser moistening the joint with water to prevent leakage. Clamp the apparatus so that the condenser is vertical with its tip reading just short of the bottom ot a 25ml measuring cylinder containing 10 ml of water and 2 ml of nitric acid which is cooled in ice and water. Add 10 ml of hydrochloric acid to the contents of the flask through the tap funnel and carefully close the tap.

Heat the flask with microburner at a rate such that the contents are brought to boiling in not less than 30 minutes. After the condenser has become full of steam, continue to heat the flask so that the distillation proceeds smoothly for 3–5 minutes. During the whole of this procedure and particularly at the moment when the steam reaches the cold water in the receiver, care should be taken to prevent a suck back.

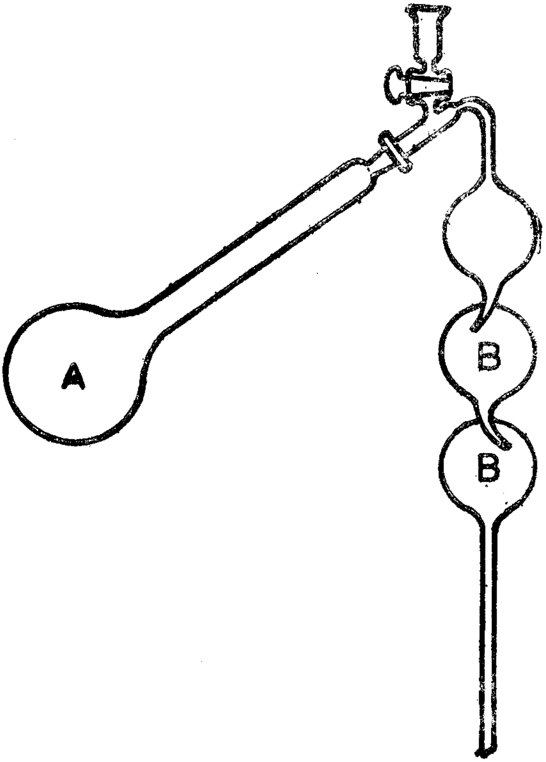

Fig. 4 Kjeldahl flask

The distillation must not be taken too far i.e. fumes of sulphur trioxide must not appear. When the distillation is complete, open the tap, remove the burner and disconnect the condenser. Wash down the condenser once with a few millimetres of water, collecting the washings in the cylinder.

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