BRITISH STANDARD

BS 4367:1968

Methods of test for

Nitric acid

Co-operating organizations

The Chemicals Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and industrial organizations:

Board of Trade
British Steel Industry
Chemical Industries Association*
Fertiliser Manufacturers' Association Ltd.*
Gas Council*
Institute of Vitreous Enamellers
Institution of Gas Engineers
Ministry of Health
National Sulphuric Acid Association
Royal Institute of Public Health and Hygiene

The industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

British Sulphate of Ammonia Federation Limited
Ministry of Defence, Army Department
National Coal Board
Pharmaceutical Society of Great Britain
United Kingdom Atomic Energy Authority

This British Standard, having been approved by the Chemicals Industry Standards Committee and endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 21 October 1968

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Contents

Foreword

This standard makes reference to the following British Standards:

BS 612, *Nessler cylinders.*

BS 975, *Density-composition tables for aqueous solutions of nitric acid.*

BS 1647, *pH scale.*

BS 1752, *Laboratory sintered or fritted filters.*

BS 1792, *One-mark volumetric flasks.*

BS 1848, *Glass condensers.*

BS 3591, *Industrial methylated spirits.*

BS 3978, *Water for laboratory use.*

BS ...., *Methods of test for sodium hypochlorite solution*[1].

The preparation of this British Standard was authorized by the Chemicals Industry Standards Committee in order to provide methods for the analysis of nitric acid of commercial quality and intended for general industrial use.

This standard prescribes methods of test only and should not be used or quoted as a specification defining limits of purity. References to the standard should be in a form of words indicating the methods of test used conform to BS 4367.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 14 and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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[1] In course of preparation.

1 Scope

This British Standard describes methods of test for commercial nitric acid suitable for general industrial purposes.

2 Determination of total acidity

2.1 Outline of method. A weighed quantity of the acid is diluted with water and titrated directly with standard sodium hydroxide solution.

2.2 Apparatus. The following apparatus is required:

1) *Pressure pipette*, as shown in Figure 1.

2) *Flask*, conical 150 ml capacity, fitted with a glass stopper.

2.3 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[2] shall be used throughout.

1) *Sodium hydroxide*, N standard volumetric solution.

2) *Bromophenol blue indicator solution*, 0.4 g/l. Warm 0.1 g of bromophenol blue with 3.0 ml of 0.05N sodium hydroxide solution and 5 ml of 95 % (v/v) ethanol[3]; after solution is effected, add 50 ml of 95 % (v/v) ethanol[3] and dilute to 250 ml with water.

2.4 Procedure. Put 30–50 ml of water into the flask, carefully dry the neck of the flask and the stopper and ensure that the outside of the flask is thoroughly dry. Replace the stopper and weigh the flask to the nearest milligramme.

Using the pressure pipette transfer about 2 ml of the sample to the flask, taking care not to allow the pipette to touch the water or sides of the flask. Immediately replace the stopper, rotate the flask to mix the contents and allow to stand for five minutes.

Momentarily withdraw the stopper to adjust the pressure. Carefully wipe the outside of the flask and reweigh to the nearest milligramme.

Add a few drops of the bromophenol blue indicator and titrate without delay with the sodium hydroxide until the colour just changes to a true blue. At the end-point, the addition of a further drop of the sodium hydroxide will produce no further change in colour.

NOTE For the highest accuracy it is essential to take into account corrections arising from calibration of the burettes and to correct the volumes of standard sodium hydroxide solution used for any deviation of temperature from that at which the solution was standardized. Relevant tables for this purpose are given in "Chemical analysis. The working tools": C. R. N. Strouts, H. N. Wilson, R. T. Parry-Jones, eds., Volume 1, page 222, Clarendon Press 1962.

2.5 Calculation. Total acidity, calculated as nitric acid, HNO_3,

$$\text{percentage by mass} = \frac{6.302 \times T_1}{M_1}$$

where T_1 = volume, in millilitres, of N sodium hydroxide solution used in the titration

and M_1 = mass, in grammes, of sample taken.

3 Determination of sulphuric acid content

3.1 Outline of method. Nitrogen acids are removed by volatilization in a current of hot air and the residual sulphuric acid is titrated with standard sodium hydroxide solution.

3.2 Apparatus. The following apparatus is required:

1) *Conical flask*, 300 ml capacity, with a suitable device to aid evaporation. One such device is shown in Figure 2; the mouth of the flask is closed by a loosely fitting, hollow, tapered closure, designed so that heated filtered air may be blown into the flask and the volatile nitrogen acids allowed to escape. The cup at the top serves as a deflector.

2) *Air line*, in which filtered compressed air is heated by passing through a coil of metal tubing immersed in boiling water.

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[2] BS 3978, "*Water for laboratory use*".

[3] Ethanol may be replaced by industrial methylated spirits, 66 degrees O.P., complying with BS 3591, "*Industrial methylated spirits*". It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations 1952 (S.I. 1952 No. 2230).

3.3 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[4)] shall be used throughout.

1) *Sodium hydroxide*, 0.1N standard volumetric solution.

2) *Hydrochloric acid*, 0.1N non-standardized volumetric solution.

3) *Bromophenol blue indicator solution*, 0.4 g/l. Warm 0.1 g of bromophenol blue with 3.0 ml of 0.05N sodium hydroxide solution and 5 ml of 95 % (v/v) ethanol[5)] after solution is effected, add 50 ml of 95 % (v/v) ethanol[5)] and dilute to 250 ml with water.

4) *Litmus paper*, neutral.

3.4 Procedure. Transfer a suitable quantity of the sample, according to the expected sulphuric acid content, to the flask and place the closure in position. Place the flask in a boiling water-bath in a fume cupboard and connect to the heated, filtered air supply. Continue passing the air until the escaping air is acid free when tested with the moistened litmus paper. Wash down the closure and the walls of the flask, using about 10 ml of water and repeat the evaporation. Again wash down with about 10 ml of water and repeat the evaporation.

To 50 ml of water add a few drops of the indicator solution and just neutralize it with the hydrochloric acid solution. Use this water to wash down the walls of the flask and the inside of the closure and collect the washings in the flask. Titrate the solution in the flask with the sodium hydroxide solution.

3.5 Calculation. Sulphuric acid content, calculated as H_2SO_4,

$$\text{percentage by mass} = \frac{0.4904 \times T_2}{V_1 \times d}$$

where d = relative density[a] of the sample at room temperature,

V_1 = volume, in millilitres, of sample taken

and T_2 = volume, in millilitres, of 0.1N sodium hydroxide solution used.

[a] Useful information is given in BS 975, "*Density-composition tables for aqueous solutions of nitric acid*".

4 Determination of nitrous acid content

4.1 Outline of method. The nitrous acid is oxidized with excess ceric sulphate solution, and the excess titrated with standard ammonium ferrous sulphate solution.

4.2 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[4)] shall be used throughout.

1) *Ammonium ferrous sulphate*, 0.1N standard volumetric solution.

NOTE This solution requires restandardization each week.

2) *Ceric sulphate*, 0.1N non-standardized volumetric solution. To 55 g of dry ammonium ceric nitrate add 50 ml of concentrated sulphuric acid (d = 1.84) and evaporate almost to dryness. Dissolve the residue in approximately N sulphuric acid solution and dilute to 1 000 ml with this acid.

3) N-*Phenylanthranilic acid indicator solution*, 2 g/l. Dissolve 0.1 g of *N*-phenylanthranilic acid in 10 ml of N sodium hydroxide solution and dilute to 50 ml with water. This solution is stable for about 1 week.

4.3 Procedure. Into a stoppered weighing bottle, weigh to the nearest milligramme, about 10 g of the sample. Transfer the weighing bottle and stopper to a wide-necked conical flask containing about 200 ml of water and 25.0 ml of the ceric sulphate solution. Swirl the flask to mix the contents, add 1 drop of the *N*-phenylanthranilic acid solution and titrate with the ammonium ferrous sulphate solution.

At the same time titrate under the same conditions 25.0 ml of the ceric sulphate solution.

4.4 Calculation. Nitrous acid content, calculated as HNO_2,

$$\text{percentage by mass} = \frac{0.235\ (T_3 - T_4)}{M_2}$$

where T_3 = volume, in millilitres, of 0.1N ammonium ferrous sulphate solution used for the 25.0 ml of ceric sulphate solution,

T_4 = volume, in millilitres, of 0.1N ammonium ferrous sulphate solution used in the determination

and M_2 = mass, in grammes, of sample taken.

[4)] BS 3978, "*Water for laboratory use*".

[5)] Ethanol may be replaced by industrial methylated spirits, 66 degrees O.P., complying with BS 3591, "*Industrial methylated spirits*". It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations 1952 (S.I. 1952 No. 2230).

5 Calculation of nitric acid content

The nitric acid content is calculated from the following formula.

Nitric acid, calculated as HNO_3,
percentage by mass = $A - 1.29\ B - 1.34$

where A = total acidity, percentage by mass, calculated as nitric acid,
B = sulphuric acid content, percentage by mass
and C = nitrous acid content, percentage by mass.

6 Determination of combined ammonia content

6.1 Outline of method. The combined ammonia present is distilled from an alkaline solution and absorbed in a solution of sulphuric acid. It is then determined spectrophotometrically using the phenoxide-hypochlorite method.

6.2 Apparatus. The apparatus required, as depicted diagrammatically in Figure 3, comprises:

1) *Kjeldahl flask*, 500 ml nominal capacity (A).

2) *Splash head with built-in tap funnel*, as detailed in Figure 4 (B).

As an alternative to the splash head (B), a separate tap funnel may be used in conjunction with a double-bulb splash head (see Figure 5).

3) *Allihn condenser*, four bulb, complying with BS 1848[6] (C).

4) *Expansion bulb*, approximate capacity 100 ml, with a delivery tube (D).

5) *Conical beaker*, nominal capacity 650 ml (E).

6) *Photoelectric absorptiometer or spectrophotometer* with 2 cm cells.

7) *Eight one-mark volumetric flasks*[7], 50 ml capacity.

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

1) *Ammonia-free water*. Prepared as follows:

Place 500 ml of tap water in a 1 litre round-bottomed flask. Add 1 ml of approximately 16N sulphuric acid. Connect the flask to a spray trap and condenser and distil. Collect the distillate in Nessler cylinders, 25 ml at a time, and test each portion with Nessler reagent.

When the distillate is free from ammonia, collect it in a glass-stoppered bottle.

Removal of ammonia from water can also be accomplished in many cases by use of a strong cation exchange resin in the H^+ form. For most work a satisfactory water can be obtained by shaking 5 litres of distilled water with 10 g of a strong cation exchange resin or by passing distilled water through a column of such an ion exchange resin.

This water shall be used throughout.

2) *Sodium hydroxide*, 300 g/l reagent solution.

3) *Sodium hypochlorite reagent solution*, 9.0 g/l available chlorine.

Prepare daily by dilution with water of a stock sodium hypochlorite solution containing 90–120 g/l of available chlorine. Standardize this solution weekly, according to the instructions given in BS ....[8].

4) Sodium phenoxide reagent solution.

a) Dissolve 62.5 g of phenol in 18.5 ml of acetone, and dilute to 100 ml with 95 % (v/v) ethanol[9] and mix.

Store this solution in the dark, preferably in a refrigerator.

b) Dissolve 27 g of sodium hydroxide in 100 ml of water.

As required, prepare the reagent by mixing 20 ml of each solution and diluting to 100 ml with water.

5) *Sodium hydroxide*, 5N non-standardized volumetric solution.

6) *Sulphuric acid*, 0.01N non-standardized volumetric solution.

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[6] BS 1848, "*Glass condensers*".

[7] BS 1792, "*One-mark volumetric flasks*".

[8] BS .... , "*Methods of test for sodium hypochlorite solution*". (In course of preparation.)

[9] Ethanol may be replaced by industrial methylated spirits, 66 degrees O.P., complying with BS 3591, "*Industrial methylated spirits*". It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations 1952 (S.I. 1952 No. 2230).

7) *Standard combined ammonia solution*. Dissolve 0.315 g of ammonium chloride in 1 000 ml of water.

Immediately before use dilute 10 ml of this solution to 100 ml with water. 1 ml of this diluted solution contains 10 µg of combined ammonia.

6.4 Procedure

6.4.1 *Preparation of colour standards*. Into five 50 ml one-mark volumetric flasks, each containing 25 ml of water, transfer amounts of the standard combined ammonia solution containing 0, 10, 20, 40 and 60 µg of ammonia and treat each solution in the following manner:

Add 8 ml of the sodium phenoxide solution and 6 ml of the sodium hypochlorite solution and mix. Dilute to the mark with water and mix. Allow to stand for 30 minutes and adjust the temperature of the solution to 25 ± 1 °C.

Measure the optical density of each solution at the wavelength of maximum absorption (approximately 620 nm[10]) against water in the reference cell, correct for the blank and prepare a calibration chart.

6.4.2 *Distillation*. Introduce 100 ml of the 300 g/l sodium hydroxide solution into the Kjeldahl flask. Dilute a suitable volume of the sample with an equal mass of water, e.g. 35 ml diluted with 50 ml of water is commonly used. Cautiously run this diluted sample into the sodium hydroxide solution through the tap funnel. Rinse the funnel with a small quantity of water and close the tap.

NOTE It is essential that the distillation is made under alkaline conditions; 100 ml of the sodium hydroxide solution is adequate for the suggested sample volume, but if this is increased a corresponding greater volume of sodium hydroxide solution should be used.

Distil about 175 ml of the liquid into the conical beaker containing 50 ml of the sulphuric acid solution. Cool the distillate, transfer to a 250 ml one-mark volumetric flask and dilute to the mark.

6.4.3 *Determination*. Transfer a suitable aliquot of the distillate to a 50 ml one-mark volumetric flask, dilute with water to about 25 ml and add 8 ml of the sodium phenoxide solution and 6 ml of the sodium hypochlorite solution, mixing after each addition. Allow to stand for 30 minutes and adjust the temperature of the solution to 25 ± 1 °C.

At the wavelength used in the calibration measure the optical density against water in the reference cell and read the amount of ammonia present from the calibration chart.

In each case carry out a blank on the reagents alone, carrying out the full distillation procedure, omitting only the sample.

6.5 Calculation. Combined ammonia content, calculated as NH_3,

$$\text{parts per million by mass} = \frac{250M_3}{V_2 \times V_3 \times d}$$

where M_3 = mass, in microgrammes, of ammonia found in the aliquot taken, corrected for any blank value,

d = relative density of the sample at room temperature,

V_2 = volume, in millilitres, of sample taken for the distillation

and V_3 = volume, in millilitres, of aliquot taken.

7 Determination of total sulphate content

7.1 Outline of method. The sulphate present is precipitated as barium sulphate and determined gravimetrically.

7.2 Apparatus. The following apparatus is required:

Sintered glass crucible, of porosity grade No. 4[11].

7.3 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[12] shall be used throughout.

1) *Sodium chloride*.

2) *Barium chloride*, 0.5M reagent solution.

3) *Hydrochloric acid*, concentrated, 36 % (m/m), 11N.

7.4 Procedure. Transfer a suitable quantity of the sample according to the expected sulphate content to a 300 ml squat form beaker, add 1 g of the sodium chloride and evaporate just to dryness in a fume cupboard. Moisten the residue with 1 ml of the concentrated hydrochloric acid and add 200 ml of boiling water. Filter, if necessary.

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[10] For use with a photoelectric absorptiometer an Ilford 607 orange filter has been found suitable.

[11] BS 1752, "*Laboratory sintered or fritted filters*".

[12] BS 3978, "*Water for laboratory use*".

Bring the solution to the boil and add dropwise 10 ml of the barium chloride solution with constant stirring. Cover the beaker and allow to stand in a warm place for four hours.

Collect the precipitate on the tared sintered glass crucible, wash the precipitate with hot water until the washings are free from chloride and dry at 150 °C. Allow to cool in a desiccator and weigh.

At the same time carry out a blank test on the reagents alone.

NOTE 1 Since this procedure involves the evaporation of considerable amounts of nitric acid, it may be advisable in some laboratories to avoid so much acid passing through the exhaust system of the fume cupboard. This can be done by concentrating the sample by distillation after the addition of the sodium chloride in an all-glass apparatus with an efficient condensation system.

NOTE 2 If there is any lead present in the sample some of the sulphate may be filtered off as lead sulphate. In normal samples of nitric acid the lead content is unlikely to be high enough to cause significant error in this determination. However, if the sample is known to have a high lead content the precipitate should be washed, gently ignited, fused with sodium carbonate and the melt dissolved in water. This solution should then be added to the main solution.

7.5 Calculation. Total sulphate content, calculated as H_2SO_4,

$$\text{percentage by mass} = \frac{42.02 \times M_4}{V_4 \times d}$$

where d = relative density of the sample at room temperature,

V_4 = volume, in millilitres, of sample taken

and M_4 = mass, in grammes, of the precipitate.

8 Determination of chloride content

8.1 Outline of method. The chloride present is determined turbidimetrically using silver nitrate.

8.2 Apparatus. The following apparatus is required:

1) *Photoelectric absorptiometer* with 4 cm cells. Alternatively *Nessler cylinders*, complying with BS 612[13].

2) *Twelve one-mark volumetric flasks*[14], 100 ml capacity.

8.3 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[15] shall be used throughout.

1) *Nitric acid*, concentrated, 70 % (m/m), 16N.

When 2 ml of the silver nitrate solution is added to 10 ml of this reagent diluted to 100 ml with water, no turbidity shall be produced.

2) *Silver nitrate*, 0.1M reagent solution.

3) *Standard sodium chloride solution*. Dissolve 1.648 g of previously dried sodium chloride in 1 000 ml water. Immediately before use further dilute 10.0 ml to 1 000 ml with water. 1 ml of the diluted solution = 10 µg Cl.

8.4 Procedure

8.4.1 *Preparation of standards*. Dilute eleven 10 ml portions of the reagent nitric acid to about 75 ml with water, ensuring that the temperature does not rise above 40 °C, and transfer each to a 100 ml one-mark volumetric flask. To the flasks, transfer amounts of the standard chloride solution, containing from 0 µg to 100 µg of chloride increasing by stages of 10 µg, and treat each solution in the following manner:

Dilute each to about 95 ml, add 2 ml of the silver nitrate solution, dilute to the mark with water, mix well and allow the solution to stand in the dark at room temperature, for not less than 5 minutes and not more than 15 minutes.

Measure the optical density of each solution in the absorptiometer using a neutral filter and prepare a calibration chart. Alternatively these standards are used directly for visual comparison.

8.4.2 *Determination*. Dilute 10.0 ml of the sample to about 75 ml with water, ensuring that the temperature does not rise above 40 °C, cool and transfer to a 100 ml volumetric flask. Dilute to about 95 ml, add 2 ml of the silver nitrate solution, dilute to the mark with water, mix well and allow the solution to stand in the dark at room temperature, for not less than 5 minutes and not more than 15 minutes.

At the same time carry out a blank test on the reagents alone.

Measure the optical densities of the solution in the absorptiometer using a neutral filter and read the amount of chloride present from the calibration chart.

Alternatively compare the turbidity of the solution with the series of the standards prepared simultaneously as described above in matched Nessler cylinders, noting the chloride content of the standard that most nearly matches the test solution.

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[13] BS 612, "*Nessler cylinders*".

[14] BS 1792, "*One-mark volumetric flasks*".

[15] BS 3978, "*Water for laboratory use*".

8.5 Calculation. Chloride, expressed as Cl,

$$\text{parts per million by mass} = \frac{0.1 \times M_5}{d}$$

where d = relative density of the sample at room temperature,

and M_5 = mass, in microgrammes, of chloride found.

9 Determination of iron content

9.1 Outline of method. The iron present is reduced to the ferrous state and determined spectrophotometrically or visually using 2,2′-bipyridyl. The method may be used in the range 10 µg to 100 µg of iron.

9.2 Apparatus. The following apparatus is required:

1) *Photoelectric absorptiometer* or *spectrophotometer* with 4 cm cells. Alternatively *Nessler cylinders* complying with BS 612[16].

2) *Thirteen one-mark volumetric flasks*[17], 100 ml capacity.

3) *One-mark volumetric flask*[17], 250 ml capacity.

9.3 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978[18] shall be used throughout.

1) *Ammonium acetate*, 200 g/l reagent solution.

2) *2,2′*-Bipyridyl, 1 g/l reagent solution. Dissolve 0.1 g of the reagent in 50 ml of water containing 2 ml of N hydrochloric acid and dilute to 100 ml.

3) *Hydroxylammonium chloride*, 100 g/l reagent solution.

4) *Hydrochloric acid*, concentrated, 36 % (m/m), 11N.

5) *Hydrochloric acid*, N reagent solution.

6) *Standard iron solution*. Dissolve 7.022 g of ammonium ferrous sulphate in a mixture of 600 ml of water and 350 ml of concentrated sulphuric acid, $d = 1.84$. Dilute to 1 000 ml with water, and further dilute 10 ml of the solution so obtained to 1 000 ml with water. 1 ml of the diluted solution contains 10 µg of iron. This final solution should be freshly prepared.

9.4 Procedure

9.4.1 *Preparation of colour standards*. Into eleven of the 100 ml one-mark volumetric flasks, each containing 50 ml of water and 2 ml of N hydrochloric acid, transfer amounts of the standard iron solution containing from 0 µg to 100 µg of iron increasing by stages of 10 µg and treat each solution in the following manner:

> Add 2 ml of the hydroxylammonium chloride solution to each and allow to stand for one minute; then add 10 ml of the ammonium acetate solution and 3 ml of the 2,2′-bipyridyl solution. Dilute the contents of each flask to 100 ml and thoroughly mix.
>
> Measure the optical density of each solution at the wavelength of maximum absorption (approximately 515 nm) against water in the comparison cell, correct for any blank and prepare a calibration chart. Alternatively these standards are used directly for visual comparison.

9.4.2 *Determination*. Measure 10.0 ml or other appropriate volume of the sample into a silica basin and evaporate just to dryness. Cool and redissolve the residue in 5 ml of the concentrated hydrochloric acid solution. Transfer to the 250 ml one-mark volumetric flask (filtering if necessary) and dilute with water to the mark. Pipette 10 ml of this solution into a 100 ml one-mark volumetric flask, add 2 ml of the hydroxylammonium chloride solution, and allow to stand for one minute. Add 10 ml of the ammonium acetate solution, mix and add 3 ml of the 2,2′-bipyridyl solution. Dilute to 100 ml with water and mix thoroughly.

At the wavelength used in the calibration measure the optical density of the solution against water in the comparison cell and read the amount of iron present from the calibration chart (see above).

Alternatively, compare the colour of the solution with the series of prepared colour standards in matched Nessler cylinders, and note the iron content of the standard that most nearly matches the test solution.

In each case carry out a blank on the reagents alone.

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[16] BS 612, "*Nessler cylinders*".

[17] BS 1792, "*One-mark volumetric flasks*".

[18] BS 3978, "*Water for laboratory use*".

9.5 Calculation. Iron content, calculated as Fe,

$$\text{parts per million by mass} = \frac{25 \times M_6}{V_5 \times d}$$

where d = relative density of the sample at room temperature,

M_6 = mass, in microgrammes, of iron found in the aliquot taken, corrected for any blank value,

and V_5 = volume, in millilitres, of sample taken.

10 Determination of lead content

10.1 Outline of method. The lead present is extracted with dithizone solution and determined spectrophotometrically. The method may be used in the range 10 µg to 100 µg of lead.

10.2 Apparatus. All glassware shall be of borosilicate glass or other glass free from lead. Reagent bottles for aqueous solutions shall be of borosilicate glass or polythene[19].

1) *Photoelectric absorptiometer* or *spectrophotometer* with 4 cm cells.

2) *Thirteen one-mark volumetric flasks*[20], 50 ml capacity.

10.3 Reagents. The reagents used shall be of a recognized analytical reagent quality selected for lead testing and all solutions shall be freshly prepared. Water complying with BS 3978[21] shall be used throughout.

1) *Chloroform*, redistilled.

2) *Dithizone reagent solution*. Dissolve 1 g of reagent in 75 ml of chloroform and filter into a 250 ml separating funnel. Shake with four successive 100 ml portions of approximately 0.2N ammonia solution. Discard the chloroform layer. Filter the combined orange coloured extracts into a 1 litre beaker and precipitate the dithizone by rendering the solution slightly acid with saturated SO_2 water. After settling, filter off the product on a sintered glass crucible and wash free from acid with water. Dry the well drained precipitate over concentrated sulphuric acid (d = 1.84) in vacuo for 3 to 4 days, in the dark. Crush the dried solid rapidly and lightly and transfer immediately to a small amber coloured bottle. The purified solid is stable for at least six months when stored in the dark.

Prepare a 0.025 g/l solution of dithizone in redistilled chloroform and transfer it to a dry stoppered amber bottle.

3) *Extraction solution*, 20 ml of 50 g/l potassium cyanide solution, and 10 ml of ammonia solution (d = 0.88) in 1 000 ml of water.

4) tri*Ammonium citrate*, 100 g/l reagent solution.

5) *Potassium cyanide*, 50 g/l reagent solution.

6) *Hydrochloric acid*, N reagent solution.

7) *Hydroxylammonium chloride*, 100 g/l reagent solution.

8) *Ammonia*, 5N reagent solution.

NOTE This solution must be freshly prepared if a large blank correction is to be avoided, since dilute ammonia dissolves lead from glass much more readily than a strong solution.

9) *Standard lead solution*. Dissolve 1.6 g of lead nitrate in water, add 1 ml of concentrated nitric acid (d = 1.42) and dilute to 1 000 ml. When required for use, take 10.0 ml of this solution, add 1 ml of concentrated nitric acid (d = 1.42) and dilute to 1 000 ml. 1 ml of the diluted solution contains 10 µg of lead.

10) *Narrow range indicator papers*, to include the pH range 8.5 to 10.0[22].

10.4 Procedure. Dithizonates are particularly sensitive to ultra-violet light and shall be shielded from direct sunlight or from fluorescent lighting in the laboratory.

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[19] It should be noted that the name "polythene" is equivalent to the name "polyethylene".

[20] BS 1792, "*One-mark volumetric flasks*".

[21] BS 3978, "*Water for laboratory use*".

[22] Defined as in BS 1647, "*pH scale*".

10.4.1 *Preparation of colour standards*. Into eleven 100 ml separating funnels, each containing 10 ml of water and 2 ml of the hydrochloric acid solution, transfer amounts of the standard lead solution, containing from 0 µg to 100 µg of lead increasing by stages of 10 µg, and treat each solution in the following manner:

> Add 1 ml of the hydroxylammonium chloride solution and 10 ml of the *tri*ammonium citrate solution and adjust the pH of the solution to between 8.5 and 10.0 by addition of the 5N ammonia solution, using the narrow range indicator papers externally. Add 2 ml of the potassium cyanide solution, and extract with 5 ml portions of the dithizone solution until the green colour is unchanged. Combine the extracts and remove the excess dithizone by extracting with the minimum quantity of the extraction solution in 5 ml portions until the colour of the chloroform solution is clear pink. Filter the chloroform solution through a small dry acid-washed filter paper[23] into a 50 ml one-mark volumetric flask, wash the paper with the chloroform collecting the washings in the flask and dilute to the mark with chloroform.
>
> Measure the optical density of each solution at the wavelength of maximum absorption (approximately 520 nm) against chloroform in the reference cell, correct for any blank and prepare a calibration chart.

10.4.2 *Determination*. Measure 5 ml of the sample into a silica dish and evaporate almost to dryness. (The amount of sample may be increased or reduced to give a colour intensity suitable for measurement; a larger sample should be taken for lead content less than 10 µg.) Dissolve the residue in 2 ml of N hydrochloric acid solution and transfer to a 100 ml separating funnel with water. Add 1 ml of the hydroxylammonium chloride solution and 10 ml of the *tri*ammonium citrate solution, and adjust the pH of the solution to between 8.5 and 10.0 by addition of the 5N ammonia solution, using the narrow range indicator papers externally. Add 2 ml of the potassium cyanide solution and extract with 5 ml portions of dithizone solution until the green colour is unchanged. Combine the extracts and remove the excess dithizone by extracting with the minimum quantity of the extraction solution in 5 ml portions until the colour of the chloroform solution is a clear pink. Filter the chloroform solution through a small dry acid-washed filter paper[23] into a 50 ml one-mark volumetric flask, wash the paper with the chloroform, collecting the washings in the flask and dilute to the mark with chloroform.

At the same time carry out a blank test on the reagents alone.

At the wavelength used in the calibration, measure the optical density against chloroform in the reference cell and read the amount of lead present from the calibration chart (see above).

10.5 Calculation. Lead content, calculated as Pb,

$$\text{parts per million by mass} = \frac{M_7}{V_6 \times d}$$

where d = relative density of the sample at room temperature,

V_6 = volume, in millilitres, of sample taken,

and M_7 = mass, in microgrammes, of lead found, corrected for any blank value.

11 Determination of sulphated ash

11.1 Outline of method. The sample is volatilized; the residue is ignited at 850 °C.

11.2 Apparatus. *Platinum dish*, about 75 mm in diameter.

11.3 Reagent. *Sulphuric acid*, 5N reagent solution.

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[23] A Whatman No. 42 paper is suitable.

11.4 Procedure. Ignite the platinum dish in a muffle furnace at 850 ± 50 °C. Cool in a desiccator and Weigh. Repeat the ignition until successive weighings do not differ by more than 1 mg. By means of a measuring cylinder, transfer 50 ml of the sample to the dish, add 1 ml of the sulphuric acid solution, cover with a watch glass supported on a glass triangle and evaporate the sample on a boiling water bath in a fume cupboard. Ignite the dish, gently at first and then for 15 minutes at 850 ± 50 °C. Cool in a desiccator and weigh. Repeat the ignition until successive weighings do not differ by more than 1 mg.

NOTE Since this procedure involves the evaporation of considerable amounts of nitric acid, it may be advisable in some laboratories to avoid so much acid passing through the exhaust system of the fume cupboard. This can be done by concentrating the sample by distillation in an all-glass apparatus with an efficient condensation system.

11.5 Calculation. Sulphated ash,

$$\text{percentage by mass} = \frac{M_8 \times 2}{d}$$

where d = relative density of the sample at room temperature,

and M_8 = mass, in grammes, of ash found.

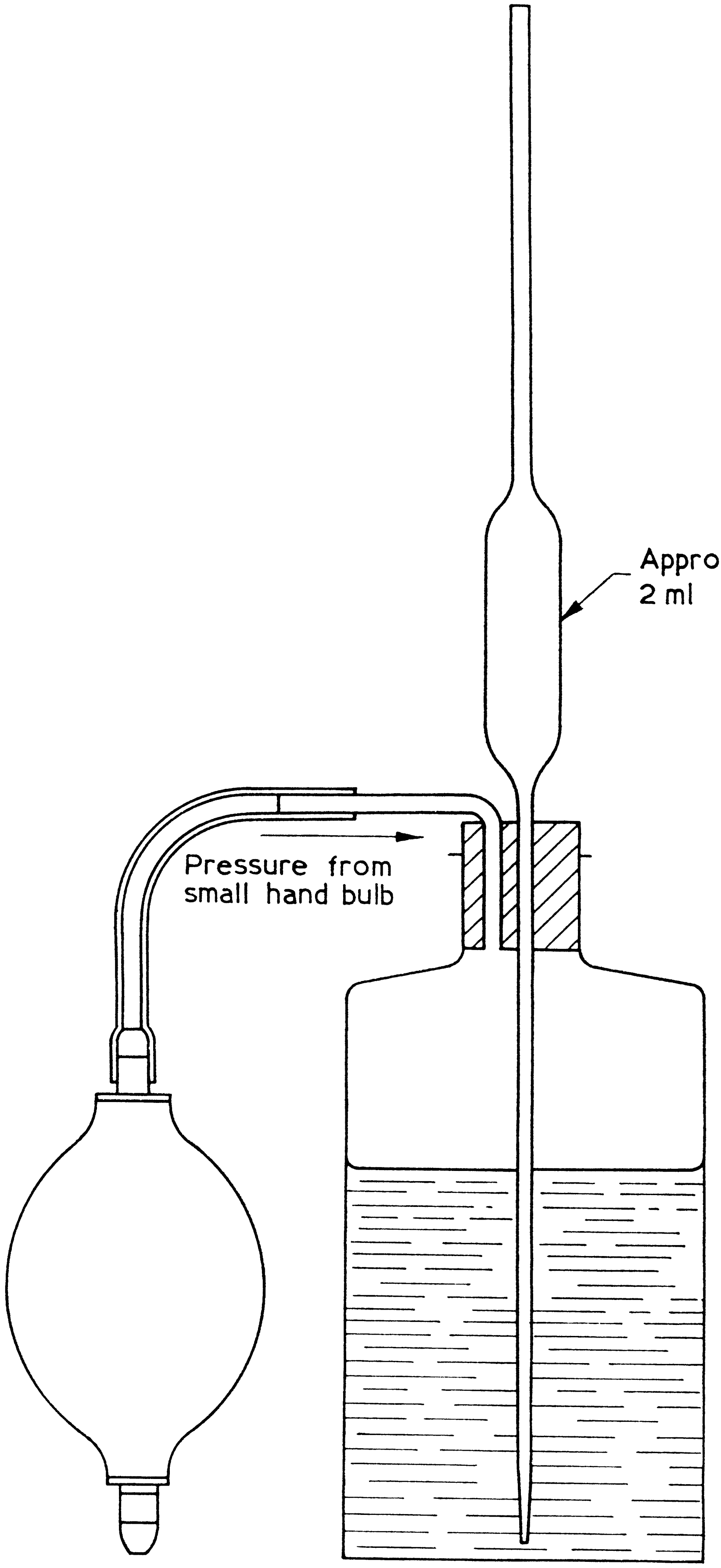


Figure 1 — Pressure pipette

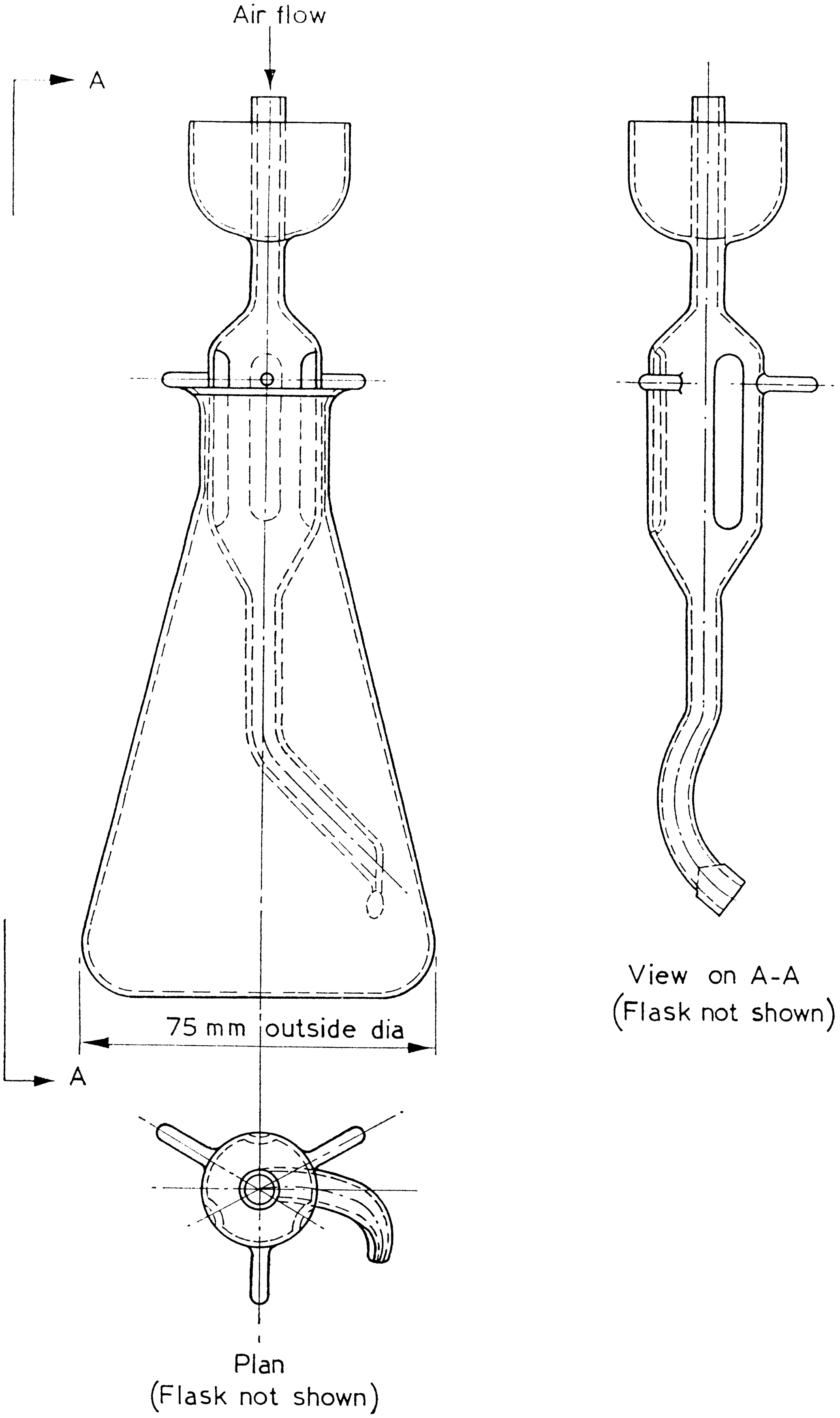


Figure 2 — Typical device for use in the determination of sulphuric acid content

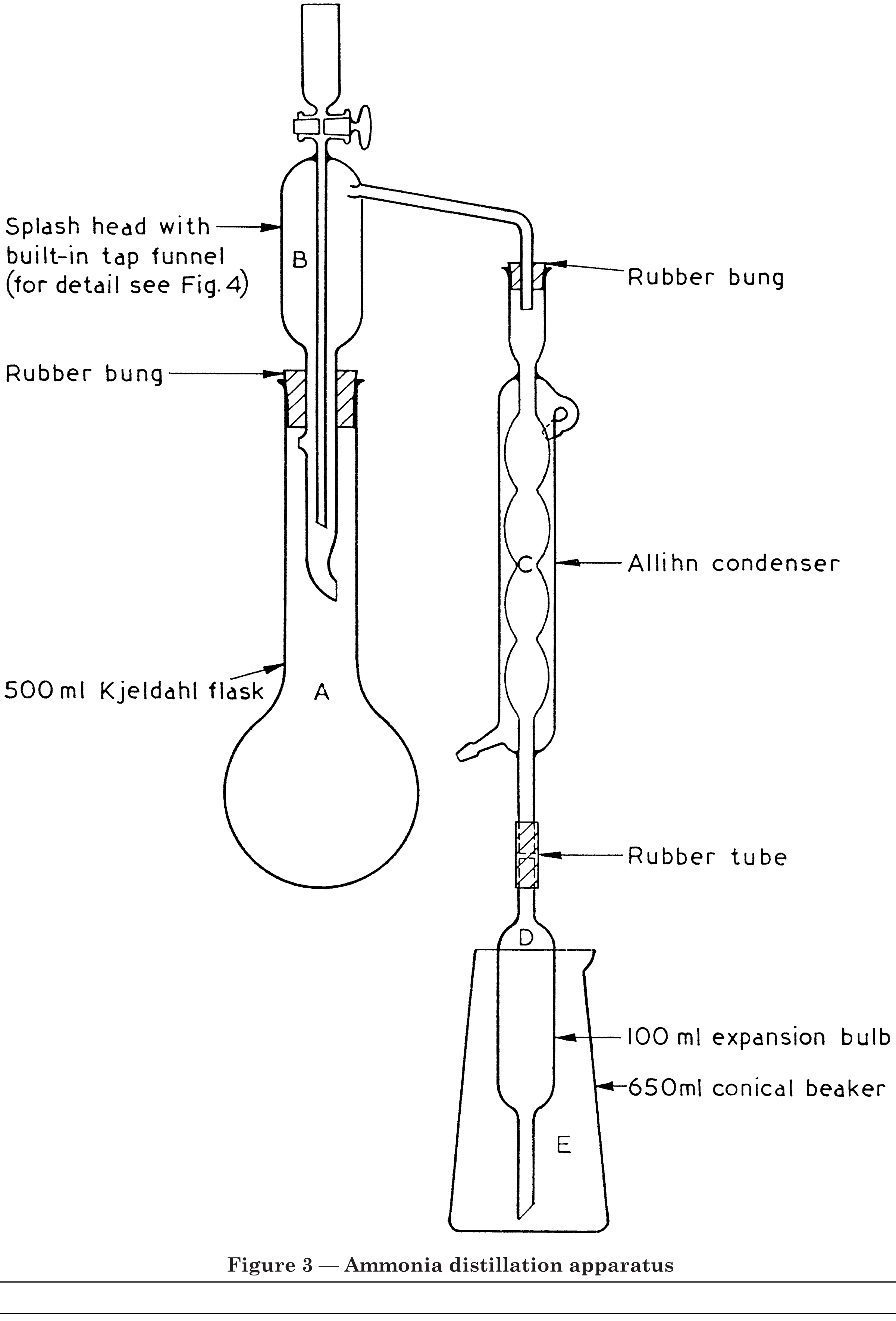
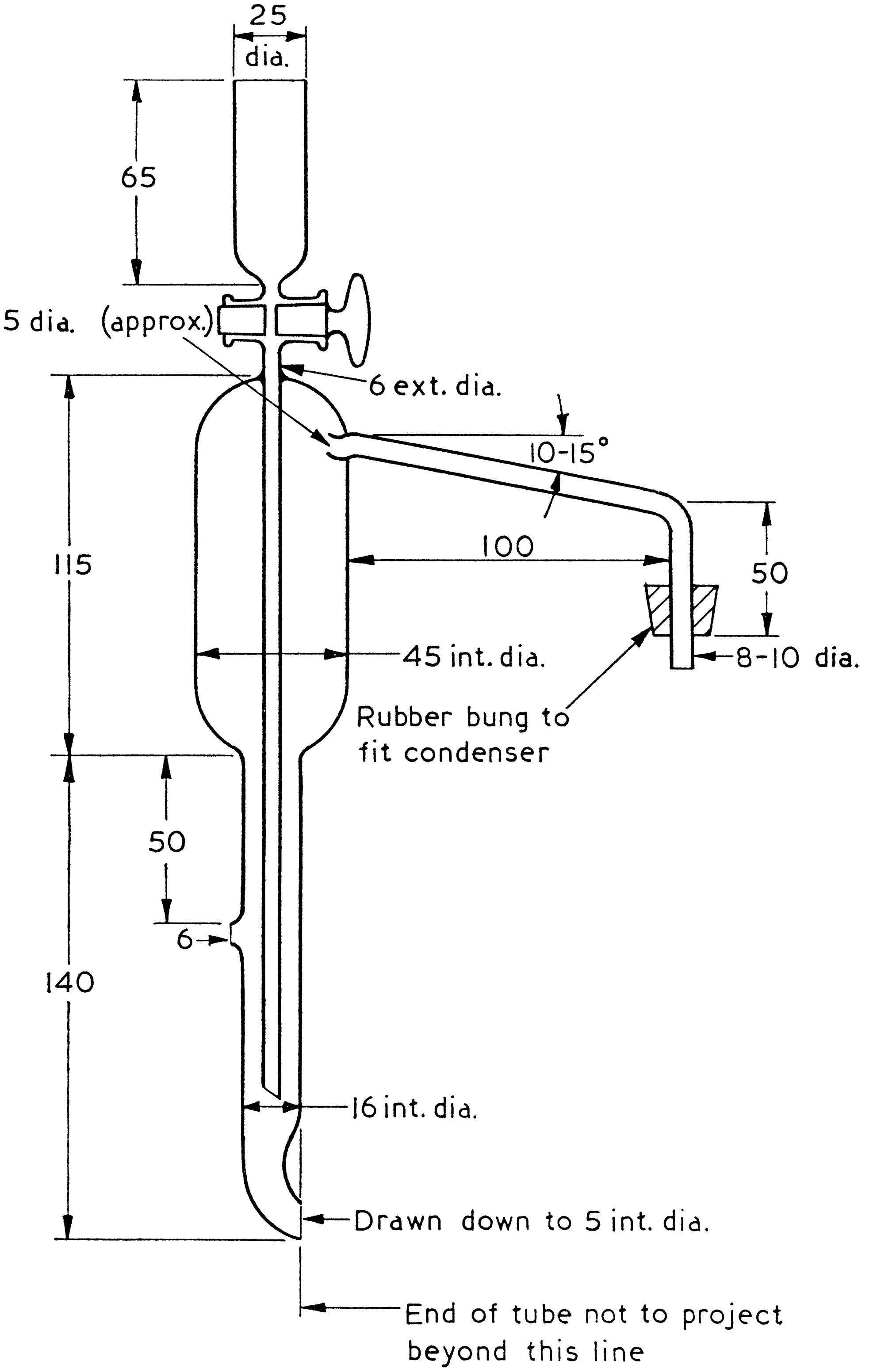
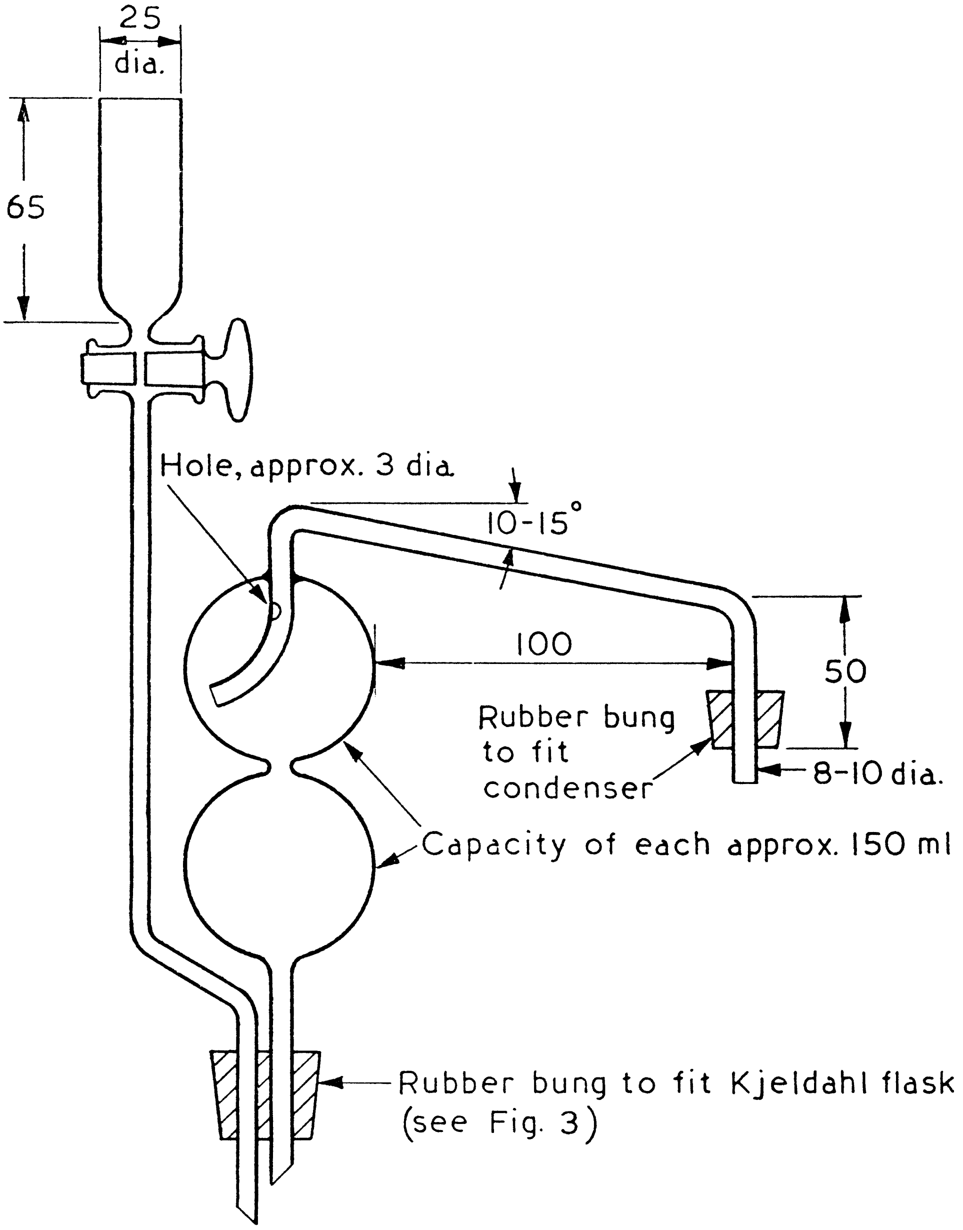


Figure 3 — Ammonia distillation apparatus



(All dimensions in millimetres)

Figure 4 — Splash head for apparatus for the distillation of ammonia



(All dimensions in millimetres)

Figure 5 — Tap funnel and double-bulb splash head

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