BRITISH STANDARD

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Specification for

Liquid chlorine

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Cooperating organizations

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

Association of Fatty Acid Distillers
Chemical Industries Association*
Department of Health and Social Security
Department of Industry — Laboratory of the Government Chemist
Fertilizer Manufacturers' Association
Institute of Vitreous Enamellers
Ministry of Agriculture, Fisheries and Food
National Sulphuric Acid Association
Royal Institute of Public Health and Hygiene
Soap and Detergent Industry Association
Society for Analytical Chemistry

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

British Fire Services Association
Electricity Supply Industry in England and Wales
Ministry of Defence
Royal Institute of Chemistry
National Water Council

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Contents

Foreword

This British Standard, prepared under the authority of the Chemicals Standards Committee, comprises a specification for liquid chlorine suitable for a range of industrial uses. It is a revision of the first edition which was published in 1965; the latter is now withdrawn.

Chlorine is a powerful irritant to the skin, mucous membrane and respiratory system. Users should consult the following publications.

a) "Precautions in handling, storage and use of liquid chlorine"; Safety and Health, new series No. 37, published by H.M.S.O.

b) "Methods for the detection of toxic substances in air, booklet No. 10, Chlorine" published by H.M. Factory Inspectorate. This provides data on the physiological response to various concentrations of chlorine gas.

c) "Codes of practice for chemicals with major hazards — Chlorine", published by the British Chemical Industries Safety Council of the Chemical Industries Association Ltd.

Because of the hazardous nature of liquid chlorine, intending users should consult the chlorine manufacturers on the design of chlorine handling equipment and on suitable operating procedures. The latter should include employee training, protective equipment, emergency measures, provision of suitable first aid equipment and procedures for vaporization and sampling.

Users are warned that it is dangerous to vaporize large quantities of liquid chlorine (for example from large storage tanks) so that the less volatile nitrogen trichloride, which on decomposition can give rise to a violent explosion, concentrates in the residues. The manufacturer should be consulted on the procedure for vaporization.

This revision incorporates (see Appendix C, Appendix D and Appendix E) two International Standards in the preparation of which the United Kingdom has been an active participant. These are both related to liquid chlorine for industrial use and are ISO 2121, ISO 2202 and ISO 2202, Addendum 1.

They form alternatives replacing the single method given in Appendix B of BS 3947:1965. Appendix A gives methods of sampling and vaporizing liquid chlorine in which the method for sampling into pressurized sample containers (**A.2**) is technically similar to the equivalent method described in ISO/R 1552.

An improved method for determination of nitrogen trichloride content is given in Appendix G.

Certification. Attention is drawn to the certification facilities described on the inside back cover.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 34, an inside back cover 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 Scope

This British Standard specifies requirements for liquid chlorine for general industrial use.

2 References

The titles of the publications referred to in this standard are listed on the inside back cover.

3 Description

Liquid chlorine is a clear yellow liquid, which on vaporizing gives a greenish yellow gas. It is gaseous at atmospheric temperatures and pressures. The chlorine supplied in the customary pressure containers is present in both liquid and gaseous phases.

4 Sampling

The methods of sampling given in Appendix A shall be used, as appropriate, for the purposes of this specification.

5 Chlorine content

The chlorine content of the vaporized liquid shall be not less than 99.5 % (*v*/*v*) when determined by the method described in Appendix B.

6 Water content

The water content of the vaporized liquid shall not exceed 100 mg/kg when determined by either of the methods described in Appendix C and Appendix D (see also Appendix E).

7 Residue on evaporation

The residue on evaporation of the liquid shall not exceed 200 mg/kg on evaporation at 20 °C, when determined by the method described in Appendix F.

8 Packaging and marking

Liquid chlorine shall be supplied only in steel containers which satisfy the recommendations of the Home Office for design, construction[1], marking, maintenance and contents limitation.

NOTE In the cases of rail and sea conveyance, the containers have also to be approved in these respects by British Rail and the Department of Trade (Marine Division) respectively under their regulations for the carriage of dangerous goods.

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[1] Attention is drawn to BS 401 and BS 349. A claim that the container complies with the requirements of BS 401 does not imply that its contents meet the requirements of BS 3947.

Appendix A Methods of sampling and vaporizing liquid chlorine and of disposing of chlorine gas

NOTE Except for the method described in **A.2**, there is no equivalent ISO method.

A.1 General

This appendix gives procedures, for use in the methods of test described in the other appendices, by means of which liquid chlorine may be sampled from a flowing stream, or from a pressure vessel, vaporized and subsequently absorbed. It comprises procedures for:

a) sampling into pressurized sample containers (**A.2**);

b) sampling into non-pressurized sample containers (**A.3**);

c) vaporization of sample from pressurized sources (**A.4**);

d) vaporization of sample from non-pressurized containers (**A.5**);

e) disposal of chlorine gas (**A.6**).

Samples should be taken from the bulk of the liquid to be sampled. In the case of chlorine supplied in containers, this can be done by using a dip tube: in the case of samples from a flowing stream, the arrangement shown in Figure 1 should be used.

Where possible, determinations should be carried out by vaporizing liquid chlorine directly from the source. If samples have to be taken, stainless steel or glass sample containers should be used.

A.2 Sampling into pressurized sample containers

NOTE This method is technically similar to the equivalent method described in ISO/R 1552.

A.2.1 *Apparatus.* The installation, shown diagrammatically in Figure 2, comprises the following.

A.2.1.1 *Sample container,* constructed of stainless steel, complying with the requirements of BS 401 and having a usable capacity of from 1 litre to 10 litres (see example in Figure 3 and Figure 4), the shorter tube having a length so calculated to give 12 % to 15 % of ullage. For the purposes of sampling, the usable capacity V, i.e. the volume from the bottom of the sample container to the lower end of the shorter tube, shall be determined initially by weighing before and after filling the sample container with water at 20 °C. The value of 1.25 V shall be inscribed on the sample container (see **A.2.2**).

NOTE Glass-lined sample containers may also be used, provided their pressure rating is adequate.

A.2.1.2 *Connection pipes and needle valves* made of chlorine-resistant materials, e.g. stainless steel. The equipment should be kept free from moisture at all times, as stainless steel is attacked by wet chlorine.

A.2.2 *Procedure.* Weigh the clean and dry sample container (**A.2.1.1**). Check that there is no blockage in the dip tube by connecting the vessel to a vacuum pump, as indicated in Figure 5, and opening both valves carefully and progressively. The rapid passage of air, observed in the sulphuric acid bubbler, indicates the absence of any blockage.

Check that the valves are functioning correctly by closing them alternately. The passage of air should then cease.

Weigh the sample container and connect it to the installation illustrated in Figure 2 with all the valves closed. Open valve V_1 to allow the chlorine to flow to valve V_2. Close valve V_1 and open valve V_2 and check the connections for gas tightness with a little soapy water. Open valves V_1 and V_3 to allow liquid chlorine to flow through the system as indicated by the arrows in Figure 2. Allow the liquid to flow for a suitable time to obtain a representative sample. Close valves V_1, V_2 and V_3 in succession and immediately open valve V_4 to allow the chlorine contained in the piping to evaporate. If necessary heat the pipes with steam. Then close valve V_4 and disconnect the sample container.

Check for correct filling of the sample container in the following manner.

Wipe away any condensation water on the outer wall and weigh the filled sample container.

The mass of the liquid chlorine sample ($M_2 - M_1$) shall not exceed 1.25 V where

M_1 is the mass of the empty sample container (kg);

M_2 is the mass of the filled sample container (kg);

V is the volume of the sample container from the bottom of the sample container to the lower end of the shorter tube (litres).

If the mass, in kilograms, exceeds the value of 1.25 V, reconnect the sample container to the sampling installation and discharge the excess of liquid chlorine by opening valve V_3.

A.3 Sampling into non-pressurized sample containers

A.3.1 ***Apparatus***

A.3.1.1 *Sampling system,* a typical example of which is shown in Figure 6, comprising:

a) two sampling flasks;

b) two vacuum-jacketed cooling baths containing a mixture of solid carbon dioxide with a suitable solvent such as trichloroethylene.

WARNING. Because of the toxicity of trichloroethylene, it is recommended that it should be handled with care and in a well-ventilated fume cupboard.

A.3.1.2 *Chlorine absorption apparatus,* as shown in Figure 9 (see **A.6**).

A.3.1.3 *Thermometer,* spirit in glass, complying with the requirements of BS 1704, type B, capable of measuring temperatures down to – 80 °C.

A.3.2 *Procedure.* Assemble the appropriate sampling flasks [**A.3.1.1** a)], connect to the appropriate chlorine source as shown in Figure 6 and immerse in the cooling mixture. Collect a suitable quantity of liquid in the first flask, maintaining the temperature of the cooling mixture at – 50 °C or lower. Close the container valve securely while the flasks are still connected and immersed in the cooling bath. Disconnect the flasks from the chlorine source and insert their stoppers.

NOTE Alcohols should not be used for cooling as they can react with chlorine to form explosive organic hypochlorites.

A.4 Vaporization of sample from pressurized sources

A.4.1 *Apparatus,* shown in Figure 8, comprising the following.

A.4.1.1 *Filter* (F), consisting of a threaded stainless steel tube approximately 6 mm internal diameter and 150 mm long, filled with glass wool.

A.4.1.2 *Stainless steel needle valve* (V_5)

A.4.1.3 *Three-way stopcock* (R_1), used as a safety by-pass valve or as a means of introducing nitrogen or air purges.

NOTE Stopcocks, etc., should be lubricated with chlorine-resistant grease. Greases based on fluorinated or chlorofluorinated products are suitable.

A.4.1.4 *Stainless steel coil,* 250 mm to 500 mm in length, 6 mm to 8 mm internal diameter, immersed in a bath of water which is heated to 80 °C by means of an electric heater (H).

A.4.1.5 *Electric heater* (H)

A.4.1.6 *Glass safety lute* (P) filled with carbon tetrachloride. Varying the height h will alter the pressure, and hence the flow rate, of chlorine gas through the connected apparatus.

A.4.2 ***Procedure***

A.4.2.1 Assemble the apparatus as shown in Figure 8.

A.4.2.2 Open the valve connecting the vaporization apparatus to the liquid chlorine source.

A.4.2.3 Turn the stopcock (R_1) and open the needle valve (V_5) to allow the chlorine to pass into the coil in the water bath. Allow the liquid chlorine sample to vaporize slowly.

A.5 Vaporization of sample from non-pressurized containers

A.5.1 *Apparatus.* As for **A.3** (see Figure 6).

A.5.2 *Procedure.* Remove the cooling bath from the second sampling flask. Allow the temperature of this flask to rise to ambient level so that any liquid chlorine contained therein will evaporate. Then remove the cooling bath from the first flask and allow the liquid chlorine sample to vaporize slowly.

A.6 Chlorine gas disposal

Dispose of chlorine gas into a safe absorption system such as is shown in Figure 9, using appropriate volumes of 200 g/l sodium hydroxide solution.

NOTE This method differs from the corresponding method described in ISO 2120 which was disapproved, for technical reasons, by the United Kingdom.

Appendix B Method for the determination of chlorine content

NOTE This method differs from the corresponding method described in ISO 2120 which was disapproved, for technical reasons, by the United Kingdom.

B.1 Principle

The liquid chlorine is vaporized and reacted with sodium chloride-potassium thiocyanate solution and the volume of gaseous impurities measured.

Any other halogens and hydrogen halides present in the sample will be wholly absorbed in the reagent and any carbon dioxide present will be partially absorbed. However, the concentrations of hydrogen chloride and carbon dioxide normally present in liquid chlorine are such that the errors due to their absorption may be neglected.

B.2 Sampling

Obtain the sample as described in **A.2**.

B.3 Vaporization

Vaporize the sample as described in **A.4**.

B.4 Chlorine gas disposal

Dispose of the excess chlorine gas as described in **A.6** using at least 500 ml of 200 g/l sodium hydroxide solution.

B.5 Reagents

The reagents used shall be of a recognized analytical quality. Water complying with the requirements of BS 3978 shall be used throughout.

B.5.1 *Sodium chloride,* saturated solution.

B.5.2 *Sodium chloride-potassium thiocyanate solution.* Dissolve about 1.4 kg of sodium chloride in 4 litres of warm water and cool to room temperature. Decant 2 litres of this saturated solution from any undissolved salt and add to it 40 g of solid potassium thiocyanate. Shake to dissolve the potassium thiocyanate and transfer to a 2 litre unstoppered aspirator to ensure saturation with dissolved air.

B.6 Apparatus

Ordinary laboratory apparatus, and

B.6.1 *Volumetric flask,* as shown in Figure 10.

B.6.2 *Flowmeter,* variable area, with a ceramic float or a capillary flowmeter capable of measuring a flow of 60 litres per hour.

B.6.3 *Aspirator,* capacity 2 000 ml.

NOTE Stopcocks etc. should be lubricated with chlorine-resistant grease. All connections should be made from chlorine-resistant material, e.g. PTFE.

B.7 Procedure

Assemble the apparatus. Connect stopcock B on the volumetric flask (**B.6.1**) to the chlorine vaporizer (Figure 8) and stopcock A, via the flowmeter (**B.6.2**), to the chlorine absorption apparatus (Figure 9) or a well ventilated fume cupboard. Pass liquid chlorine through the vaporizer, at such a rate as to give a gaseous chlorine flow rate of 60 litres per hour through the volumetric flask, for a period of 20 min to displace all the air from the system. Close stopcock A of the volumetric flask, allowing a small positive pressure to build up within the flask. After 5 s, turn stopcock B so that the flask is isolated and the vaporizer is connected to a suitable venting system. Immediately stop the liquid chlorine supply and allow any liquid chlorine remaining in the vaporizer to vaporize through the venting system.

Do not allow the chlorine to vaporize into a closed system for more than a few seconds, as the pressure developed may cause escape of liquid chlorine from the apparatus.

Allow the volumetric flask containing the test portion to stand for at least 10 min in order to attain ambient temperature. Attach a levelling bottle, containing saturated sodium chloride solution, at the open capillary side of stopcock A. Fill the capillary arms and bore of the stopcock with the solution. Place a small beaker containing saturated sodium chloride solution in a position such that the end of the capillary tubing lies just below the surface of the liquid. Open stopcock A through to the beaker and allow the sample to bubble through the solution until atmospheric pressure is attained within the volumetric flask. Close stopcock A and remove the beaker and levelling bottle. It is important that the body of the flask should not be handled during the above procedure.

Attach the aspirator (**B.6.3**), containing the sodium chloride-potassium thiocyanate reagent, to the inlet of the stopcock B by means of suitable flexible tubing. Clamp the volumetric flask at an angle of about 30° to the horizontal so that the stopcock B is pointing downwards and clamp the reagent aspirator in a position slightly above the flask. Open the stopcock of the aspirator and turn stopcock B so as to flush all air from the connecting tube and from the bore of stopcock B. When all air has been removed, turn stopcock B so as to allow reagent to enter the volumetric flask and react with the chlorine. It is important that the reaction is carried out using a small positive head of reagent at all times.

When the reaction is apparently complete (after about 5 min), close stopcock B and invert the flask several times in order to remove any remaining traces of chlorine. Finally, open stopcock B through to the aspirator and note the volume of residual gas when levelled off to atmospheric pressure.

B.8 Expression of results

Chlorine content, expressed as percentage by volume, is given by the formula:

$$100 - \frac{V_1 \times 100}{V_2}$$

where

V_1 is the volume of residual gas (ml);

V_2 is the capacity of the volumetric flask (ml).

Appendix C Method for the determination of water content: gravimetric method

NOTE This method is technically identical with that described in ISO 2121.

C.1 General

This appendix describes a gravimetric method for the determination of the "volatile water", i.e. that which volatilizes at the same time as the chlorine during the gasification of liquid chlorine for industrial use.

C.2 Field of application

This method should not be used with samples taken in steel containers subject to corrosion in that the hygroscopic ferric chloride so formed will absorb water and invalidate the result of the determination.

C.3 Principle

The water is absorbed by passing the gasified sample into tared absorbers containing phosphorus (V) oxide or magnesium perchlorate.

The gaseous chlorine and any volatile impurities, other than water, are eliminated by flushing the absorbers with dry air or nitrogen heated to 80 °C.

The chlorine leaving the absorbers is passed through a tared bottle containing sodium hydroxide solution.

The absorbers and the bottle containing the sodium hydroxide solution are reweighed and the mass of water and that of the chlorine sample are obtained by difference.

C.4 Sampling

Obtain the sample as described in **A.2** or directly via a vaporizer (Figure 8) from a flowing stream (Figure 1).

C.5 Vaporization

Vaporize the sample as described in **A.4**.

C.6 Reagents

The reagents used shall be of laboratory grade and water complying with the requirements of BS 3978 shall be used throughout.

C.6.1 *Absorbent.* Choose either

C.6.1.1 *Phosphorus (V) oxide*, or

C.6.1.2 *Magnesium perchlorate,* granules in the size range 3 mm to 5 mm (to avoid loss of material during the absorption of water) and containing not more than 2 molecules of water of crystallization, i.e. 13.9 %, as determined by the method given in **C.10**.

Magnesium perchlorate should not be used if the presence of organic matter is suspected.

C.6.2 *Air or nitrogen,* dry.

C.6.3 *Sodium hydroxide,* 200 g/l solution, approximately 5N.

C.6.4 *Iodized starch indicator,* 2 g/l starch solution containing 40 g of potassium iodide and 4 g of sodium hydrogen carbonate per litre.

C.6.5 *Acetone*

C.6.6 *Chlorine-resistant grease.* Greases based on fluorinated or chlorofluorinated products are suitable.

C.7 Apparatus

The apparatus, shown diagrammatically in Figure 12, comprises the following.

C.7.1 *Bottle* (A), containing 2.5 litres of the sodium hydroxide solution (**C.6.3**) for absorbing the test portion of chlorine used.

C.7.2 *Bubbler* (C), containing about 100 ml of the iodized starch indicator (**C.6.4**) for detection of chlorine breakthrough.

C.7.3 *Safety bottle* (G).

C.7.4 *Flowmeter* (F), variable area, with a ceramic float or a capillary flowmeter capable of measuring a flow of 60 litres per hour.

C.7.5 *Stopcock* (R_2).

C.7.6 *U-tubes* T_1, T_2, T_3 and E, each about 80 mm in height, made of 12 mm o.d. standard wall glass tube, with ground glass stopcocks. Three of the tubes (T_1, T_2 and T_3) contain the phosphorus (V) oxide (**C.6.1.1**) or the magnesium perchlorate (**C.6.1.2**) covered by a wad of glass wool in each of the two branches. Each loaded tube, weighed separately, should have a mass of not more than 100 g. All connections should be of chlorine-resistant tubing and kept as short as possible. The U-tube (E), fitted with ground glass joints, should be filled with glass wool previously dried in an oven at 110 °C for 1 h.

C.7.7 *Flexible connections,* of chlorine-resistant tubing.

C.8 Procedure

C.8.1 *Preliminary operations.* Clean the U-tubes T_1, T_2 and T_3, first with water, then with acetone (**C.6.5**) and dry them. Fill them with the absorbent (**C.6.1**), coat the stopcocks with a little of the chlorine-resistant grease (**C.6.6**) and connect the absorber tubes in the apparatus, as shown in Figure 12, to the chlorine vaporizer (Figure 8) and thence to the chlorine supply (Figure 1 or Figure 2).

When the absorber tubes are freshly charged, condition them by passing gaseous chlorine at a rate of 25 litres per hour for 2 h in order to allow the chlorine to react with certain impurities in the absorbent. Unless this is done, the first result will be in excess of the correct value.

Close the chlorine feed valve V_1 (Figure 1) or V_2 (Figure 2) to turn off the chlorine supply to the vaporizer (Figure 8). Operate the stopcock R_1 to purge the apparatus with dry air or nitrogen (**C.6.2**).

Flush the absorber tubes for 10 min at the rate of 25 litres per hour with the dry air or nitrogen, heated to about 80 °C by the chlorine vaporizer, to eliminate any volatile impurities, other than water, remaining in the absorber tube.

Remove the hot water bath and flush for a further 5 min with the same gas at room temperature.

Then close stopcocks R_1 (Figure 8) and R_2 (Figure 12) and those on the absorber tubes. Disconnect the absorber tubes T_1, T_2 and T_3 (Figure 12), and weigh them separately, to the nearest 0.1 mg.

Replace the absorber tubes in the apparatus and open all the stopcocks on the U-tubes.

Replace the 2.5 litres of the sodium hydroxide solution (**C.6.3**) in the bottle A, weigh complete to the nearest 0.5 g, and reassemble the apparatus.

C.8.2 *Determination.* Turn on the chlorine supply and turn the stopcock R_1 (Figure 8) so as to allow the filtered and subsequently vaporized chlorine to flow towards the safety lute P (Figure 8). Then open the stopcock R_2 (Figure 12) to allow the chlorine gas to enter the absorption train at a flow rate of 25 litres per hour.

Allow about 100 litres of the chlorine gas to pass into the absorption train. Weigh the bottle A, complete, after the determination and calculate the mass of absorbed chlorine.

During the determination, which lasts about 4 h, it is essential that all chlorine gas passed through the tubes be totally absorbed. Such is the case if the iodized starch indicator (**C.6.4**) in the bubbler (**C.7.2**) does not develop an intense blue colour.

When sufficient chlorine has been passed, turn off the chlorine supply and adjust the stopcock R_1 (Figure 8) to purge the apparatus for 10 min at the rate of 25 litres per hour with dry air or nitrogen heated to about 80 °C by the chlorine vaporizer. Remove the hot water bath and continue the flushing for a further 5 min with the same gas at room temperature, then close stopcocks R_1 (Figure 8) and R_2 (Figure 12) and those on the absorber tubes.

Disconnect the absorber tubes, T_1, T_2 and T_3, and reweigh them separately to the nearest 0.1 mg.

Normally, the water is completely absorbed in the tube T_1. If the tube T_2 shows an increase in mass of more than 20 % of the quantity absorbed in T_1, repeat the determination after recharging T_1 and reconditioning the tube by the method described in **C.8.1**, paragraph 2.

T_3 will likewise indicate when the contents of T_2 require renewal and also act as a safeguard. The increase in mass of the third tube (T_3) should not exceed 2 mg.

NOTE To obtain reproducible results it is necessary, each time, to pass the gas in the same direction through the tubes, to place the tubes in the same order and to treat the tubes in the same way before each weighing, e.g. by wiping with a chamois leather.

C.9 Expression of results

Water content, expressed in milligrams per kilogram of chlorine, is given by the formula:

$$\frac{m_1 \times 10^6}{m + m_1}$$

where

m_1 is the mass of the weighed water in the absorber tubes T_1, T_2 and T_3 (**C.7.6**), i.e. the difference between the masses of the absorbers before and after passage of the chlorine (g);

m is the mass of chlorine in the test portion, i.e. the difference in the mass of the sodium hydroxide absorption bottle A (**C.7.1**) before and after the determination (g).

Express the results to the nearest unit.

C.10 Method for checking the degree of hydration of the magnesium perchlorate used as drying agent in the determination of water content of chlorine

C.10.1 *Principle.* The increase in temperature resulting from the dissolution of the magnesium perchlorate in water is measured. The water content is ascertained from a calibration graph which plots the water content of magnesium perchlorate against the increase in temperature resulting from its dissolution.

C.10.2 ***Apparatus***

C.10.2.1 *Silvered Dewar flask,* of about 60 mm internal diameter, 100 mm high and of 300 ml capacity.

C.10.2.2 *Thermometer,* complying with the requirements of BS 1704, covering the range 0 to 100 °C, graduated at each 1 °C interval.

C.10.2.3 *Waxed cork stopper,* pierced with a hole to take the thermometer and intended to form a stopper for the Dewar flask (**C.10.2.1**).

C.10.2.4 *Filter paper cylinder,* 40 mm in diameter and 75 mm high, open at the top, made from a rectangular sheet of filter paper measuring 100 mm × 150 mm, rolled on a suitable former and turned in towards the bottom to form the base, the whole being held in shape with adhesive paper.

C.10.2.5 *Graduated measuring cylinder,* 100 ml, complying with the requirements of BS 604.

C.10.3 ***Procedure***

C.10.3.1 *Test portion.* At the moment of use weigh, to the nearest 0.1 g, 20 g of magnesium perchlorate in the filter paper cylinder (**C.10.2.4**) and close the cylinder by folding the paper.

C.10.3.2 *Determination.* Pour 75 ml of water into the Dewar flask (**C.10.2.1**). Close the flask with the waxed cork (**C.10.2.3**) fitted with the thermometer (**C.10.2.2**) and read the temperature of the water when equilibrium is reached.

Place the filter paper cylinder (**C.10.2.4**) containing the test portion (**C.10.3.1**) in the Dewar flask (**C.10.2.1**) and replace the cork. Shake with a gentle circular movement to aid dissolution of the product and read the temperature when it reaches equilibrium (i.e. after 20 s to 25 s).

C.10.4 *Expression of results.* Ascertain from Figure 11 the water content of the magnesium perchlorate, as a percentage by mass, corresponding to the increase in temperature observed at the time of dissolution.

Appendix D Method for the determination of water content using an electrolytic analyser

NOTE This method is technically identical with that described in ISO 2202.

D.1 General

This appendix describes an electrolytic method for the determination of the "volatile water", i.e. that which volatilizes at the same time as the chlorine, during the vaporization of liquid chlorine for industrial use.

D.2 Field of application

This method should not be used with samples taken in steel containers subject to corrosion in that hygroscopic ferric chloride formed will absorb water and invalidate the results of the determination.

D.3 Principle

The water in the vaporized chlorine is continuously absorbed in an electrolytic cell where it is decomposed by electrolysis. The electrolytic current, which is a function of the water content, is measured.

D.4 Sampling

Obtain the sample as described in **A.2** or directly via the vaporizer (Figure 8) from the flowing stream (Figure 1).

D.5 Vaporization

Vaporize the sample as described in **A.4**.

D.6 Reagents

The reagents used shall be of a recognized analytical quality. Water complying with the requirements of BS 3978 shall be used throughout.

D.6.1 *Sulphuric acid,* $p = 1.71$ g/ml, 78.5 % (*m*/*m*) solution, or any other sulphuric acid solution of known concentration between 76 % and 85 % (*m*/*m*).

D.6.2 *Desiccant,* resistant to chlorine (e.g. silica gel).

D.6.3 *Dry nitrogen,* with water content less than 10 ml/m^3.

D.6.4 *Chlorine-resistant grease.* Greases based on fluorinated or chlorofluorinated products are suitable.

D.7 Apparatus

The apparatus, shown diagrammatically in Figure 13, is commercially available.

The gas circuit is made of borosilicate glass tubing about 3 mm to 5 mm internal diameter having only greased ground joints (see **D.6.4**), or joints constructed from fluorocarbon polymer.

The apparatus includes seven glass stopcocks, R_2 to R_8, all having inserts made from fluorocarbon polymeric material.

The apparatus comprises the following.

D.7.1 *Bubbler* (A), used for checking the analyser, containing sufficient sulphuric acid solution (**D.6.1**) to immerse all the sintered glass plates under the conditions of use.

D.7.2 *Thermostatic sheath* (B), for the bubbler.

D.7.3 *Long-stem precision thermometer* (T), including the range 15 °C to 30 °C, accurate to ± 0.1 °C.

D.7.4 *Safety flask* (C).

D.7.5 *Gas flowmeter* (D), for reading gaseous chlorine flow rates between 0 and 1 000 ml/min.

D.7.6 *Gas flowmeter* (E), for reading gaseous chlorine flow rates between 0 and 150 ml/min.

D.7.7 *Filter* (F), made of sintered glass (pore diameter between 90 µm and 150 µm), for protecting the electrolytic cell (H).

D.7.8 *Electrolytic cell* (H), comprising, for example, a borosilicate glass rod, on which two electrodes, usually platinum, are wound over the entire length and between which is applied a thin film of phosphorus (V) oxide. This element is enclosed in a glass envelope protected from external moisture by a guard tube containing the desiccant (**D.6.2**). The whole should be capable of being readily dismantled and cleaned for regenerating the cell.

D.7.9 *Ammeter* (I), multirange instrument capable of discriminating 50 µA and having a maximum reading of at least 10 mA, fitted in such a way that it can be short-circuited while the electrolytic cell is being dried, in order to protect the meter.

D.7.10 *Constant direct voltage source* (K), about 50 V. A battery source is suitable.

D.7.11 *Safety tube* (G), containing the desiccant (**D.6.2**).

D.7.12 *Recorder* (P) (optional), for the continuous measurement of the electrolytic current.

D.8 Procedure

D.8.1 *Installation and preliminary operation.* Install the analyser as near as possible to the chlorine source. Completely clean all lines, first with water and then with acetone, in order to remove all particles that might affect the performance of the cell and dry by flushing with the dry nitrogen (**D.6.3**).

Assemble the apparatus as shown in Figure 13 and connect it to the chlorine vaporizer (Figure 8) and the chlorine supply (**D.4**). Open valve R_2.

Close stopcocks R_3, R_5 and R_7, and open stopcocks R_4, R_6 and R_8.

Connect the electrolytic cell. The voltage is not critical, but should not exceed 70 V. Operate the stopcock R_1 (Figure 8) so as to admit the dry nitrogen (**D.6.3**) to the analyser at a rate of 500 ml/min to 1 000 ml/min, measured on the flowmeter (D).

After approximately 15 min, adjust stopcocks R_6 and R_7 so as to pass part of the nitrogen to the electrolytic cell (H) at a rate such that the current does not exceed 10 mA. If necessary, reduce or even stop the nitrogen supply. Then regulate the flow to 100 ml/min, measured by the flowmeter (E).

Wait until the ammeter (I) indicates a value corresponding to less than 10 ml/m^3 of water, i.e. less than 132 µA. Close stopcock R_1 (Figure 8).

D.8.2 *Checking.* In principle, the analyser does not require calibration. However, it can be checked by the following procedure using the chlorine to be analysed from the vaporizer (see Figure 8) after having adjusted the flow, by means of valve V_5 (Figure 8), to give a total gas flow rate greater than 100 ml/min, measured by the flowmeter (D).

Open stopcocks R_3 and R_5, and close R_4 so as to pass the gas into the bubbler containing the sulphuric acid solution (**D.6.1**).

Open stopcock R_7 and adjust stopcock R_6 in order to pass exactly 100 ml of gas per minute, measured by the flowmeter (E) into the electrolytic cell (H).

Record the electric current after it has remained constant for at least 10 min, and the temperature on the thermometer (T).

The water content obtained should be within 10 %, in relative value, of that indicated in the graph (Figure 14) for the concentration and temperature of the sulphuric acid solution (**D.6.1**) in the bubbler (A).

D.8.3 *Determination.* Having installed and dried the apparatus as described in **D.8.1**, close stopcocks R_3, R_5 and R_7, and open R_4 and R_8. Connect to the chlorine vaporizer and thence to the chlorine supply (Figure 1 or Figure 2). Open stopcock R_1 (Figure 8) and adjust the flow, by means of valve V_5, to 500 ml/min to 1 000 ml/min, measured by the flowmeter (D), for approximately 15 min.

Cautiously open stopcock R_7 and partially close R_6, passing the chlorine to be analysed into the electrolytic cell (H) at a rate such that the current does not exceed 10 mA. If necessary, reduce the flow of chlorine into the cell until a satisfactory reading can be obtained.

Regulate the chlorine flow rate through the cell to 100 ml/min, measured by the flowmeter (E).

Record the electric current after it has remained constant for at least 10 min.

D.8.4 *Checking the performance of the apparatus.* Two sets of factors can affect performance of the phosphorus (V) oxide cell.

D.8.4.1 Contamination by very fine particles of conducting material not held back by the filter (**D.7.7**) or introduced accidentally whilst setting up the apparatus. This causes short-circuiting between the electrodes, and subsequent cell failure.

It is then necessary to replace the cell.

D.8.4.2 Slow poisoning of the phosphorus (V) oxide by gaseous or liquid impurities entrained by the chlorine which are capable of reacting with the phosphorus (V) oxide or of being absorbed on its surface. This causes a gradual reduction in sensitivity, a slower response rate and faulty results.

It is therefore necessary to check periodically that the performance of the analyser complies with the following requirements.

D.8.4.2.1 The water content observed on reducing the chlorine rate to half should be half the initial value, with a maximum relative deviation of 10 %. If the observed value greatly exceeds half the initial value, it is possible that the apparatus has been contaminated by extraneous moisture.

D.8.4.2.2 The ammeter reading should always return close to zero when the flow of chlorine is cut off for approximately 30 min and then rise to within 10 % (in relative value) of its initial value, on restoring the flow.

D.8.4.2.3 The ammeter reading should return to within 10 % (in relative value) of its initial value after stabilizing, when the electrolysis current has been interrupted and then restored after 3 min to 5 min.

If the results of these checks are not satisfactory, replace the cell.

D.9 Expression of results

It is convenient in practice to graduate the ammeter directly in terms of water content.

Calculation of the water content, as a function of current obtained, is carried out in accordance with the following data.

96 500 coulombs correspond to 1 gram-equivalent of water.

96.5 coulombs correspond to 1 milligram-equivalent of water.

96.5 × 2 = 193 coulombs correspond to 1 mmol of water.

Hence

1 coulomb corresponds to the electrolysis of

$$\frac{18.016}{193} = 0.0933 \text{ mg of water, or}$$

$$\frac{24.3}{193} = 0.1258 \text{ ml of water vapour at } 20\ ^\circ\text{C and } 100 \text{ kPa.}$$

If the chlorine is passed to the cell at a rate of 100 ml/min, or $\frac{100 \times 10^{-6}}{60}$ m^3/s, a current of 1 μA would correspond to the following water contents in the gas:

$$0.1258 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} = 0.0755 \text{ ml/m}^3.$$

$$0.0933 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} = 0.0560 \text{ mg/m}^3.$$

$$0.0933 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} \times \frac{1}{2.99} = 0.0187 \text{ mg/kg.}$$

where

2.99 is the unit mass of the gaseous chlorine at 20 °C and 100 kPa, that is, for the conditions of analysis.

The following data may be used in assessing the sensitivity of the method.

1 ml of water vapour/m^3 of gas corresponds to a current of $\frac{1}{0.0755}$ = 13.24 µA.

1 mg of water/m^3 of gas corresponds to a current of $\frac{1}{0.0560}$ = 17.9 µA.

1 mg of water/kg of gas corresponds to a current of $\frac{1}{0.0187}$ = 53.5 µA.

Appendix E Alternative method of calibration of the electrolytic cell for the determination of water content

NOTE This method is technically identical with that described in Addendum No. 1 to ISO 2202.

E.1 General

This appendix describes a simple and rapid procedure for checking the ageing of the electrolytic cell used for the determination of water in liquid chlorine. It is possible to calculate rapidly the output of the cell, the working life of which can thus be extended until the output falls to 75 % or even less, before the cell need be replaced or regenerated.

E.2 Principle

A known volume of solvent, the water content of which has been pre-determined by the Karl Fischer method (see BS 2511) is injected into the gas to be analysed. After approximately 15 min, the area of the peak appearing on the recorder chart is measured.

The output of the electrolytic cell is calculated by relating the number of coulombs corresponding to this area to the theoretical number of coulombs required to electrolyse the quantity of water injected.

E.3 Reagents

Solvent of known water content, such as 1,2-dichloroethane, which has a water content of about 1 g/l. This content should be determined by the Karl Fischer method (see BS 2511).

E.4 Apparatus

The apparatus, shown diagrammatically in Figure 15, is similar to that described in Appendix D, but includes the following additional components.

E.4.1 *Syringe* (S), 100 µl, containing the solvent (**E.3.1**), fitted with a needle, L_1, of internal diameter 0.18 mm, for injecting the solvent into the gas being analysed.

E.4.2 *Injection chamber* (J) (T-tube), into which the solvent of known water content is injected for the check test.

E.4.3 *Septum* (M), silicone-based, resistant to chlorine and free from water, pierced by the needle L_1. This septum is placed over the opening of the injection chamber (vertical part of the T-tube) and is held in position by a washer and screw cap.

E.4.4 *Recorder* (P), for the continuous measurement of the electrolytic current.

The solvent is drawn off by an apparatus, shown diagrammatically in Figure 16, comprising the following.

E.4.5 *Two-necked flask* (B), approximately 100 ml capacity, one neck fitted with a ground glass stopper and the other with a three-way stopcock, R_9, through which a needle L_2 passes. This needle can be attached to the syringe (**E.4.1**), enabling the solvent to be drawn off under a flow of dry nitrogen introduced through the side tube of stopcock R_9.

E.4.6 *Needle* (L_2), of internal diameter 0.30 mm, used for filling the syringe (**E.4.1**).

E.5 Procedure

Assemble the apparatus and use it to carry out the determinations described in Appendix D. To check the analyser, ensure that the observed water content on the recorder (**E.4.4**) remains stable for at least 15 min.

Fill the syringe (**E.4.1**) as follows.

Detach the syringe from the needle L_1 without withdrawing the latter from the septum M and attach the syringe to the needle L_2. Insert this needle through stopcock R_9 into the flask (**E.4.5**) containing the solvent. During this operation, pass a current of dry nitrogen through stopcock R_9 so as to prevent the ingress of moisture. Rinse the syringe three times with the solvent, which is discarded each time, fill it and attach it again to the needle L_1.

Rinse the needle L_1 by injecting a preliminary volume of about 10 µl of the solvent (**E.3.1**) into the injection chamber (**E.4.2**) and wait until the observed water content on the recorder returns to its original value.

Then place a suitable volume of the solvent (**E.3.1**) in the injection chamber for the blank test (usually 20 µl when its water content is of the order of 1 g/l, corresponding to 20 µg of water).

Wait until the current, read on the recorder, has returned practically to its initial value, which is generally after about 15 min.

Calculate the output of the electrolytic cell from the recorder chart, as indicated in **E.6**. An example of a recorder chart is given in Figure 18.

In practice it is possible to maintain the working life of an electrolytic cell when it undergoes a slow and regular reduction in sensitivity until its output has dropped to as low as 75 %, before regenerating or replacing it.

E.6 Expression of results

E.6.1 The performance *R* of the electrolytic cell, expressed as a percentage, is given by the formula:

$$R = 100 \times \frac{C_1}{C}$$

where

C and C_1 are respectively the number of coulombs required theoretically and in practice for the electrolysis of the quantity of water injected.

These values of C and C_1 are calculated as shown in **E.6.2** and **E.6.3**.

E.6.2 $C = 96.5 \times \frac{m}{9.008}$

where

96.5 is the number of coulombs corresponding to 1 milligram-equivalent of water;

9.008 is the mass of 1 milligram-equivalent of water (mg);

m is the mass of water injected (mg).

E.6.3 $C_1 = I \times t \times \frac{S_1}{S}$

where

I is the current corresponding to the highest reading of the recorder scale (A);

NOTE $I = 0.002$ A (in the example shown in Figure 18).

t is the time of the recording(s);

$\frac{S_1}{S}$ is the ratio of the area of the recorder peak (hatched part of Figure 18) to the total area of the rectangle $I \times t$. This ratio can be determined by calculation, by weighing the cut-out areas or by any other means.

Example of calculation relating to the diagram shown in Figure 17.

$m = 0.020$ mg of H_2O

$$\frac{S_1}{S} = \frac{\text{the mass of the hatched area of graph paper}}{\text{the mass of the graph paper equivalent to } I \times t}$$

$$= \frac{0.246}{2.478} = 0.099$$

$I = 0.002$ A

$t = 15 \times 60$ s $= 900$ s

Hence

$$C = 96.5 \times \frac{0.020}{9.008} = 0.2142 \text{ coulombs}$$

$$C_1 = 0.002 \times 900 \times 0.099 = 0.1786 \text{ coulombs}$$

$$R = 100 \times \frac{0.1786}{0.2142} = 83.3\ \%.$$

Appendix F Method for the determination of residue on evaporation

NOTE There is no equivalent ISO method.

F.1 Principle

The liquid chlorine is vaporized and the residue, after evaporation, is weighed.

F.2 Sampling

Obtain the sample as described in **A.3** (see Figure 6).

F.3 Apparatus

As described in **A.3.1** using 250 ml sample flasks (Figure 7B. and:

F.3.1 *Flowmeter,* capable of measuring 250 ml per minute of dry air.

F.4 Procedure

Dry the 250 ml sample flasks [**A.3.1.1** a)] in an oven at 105 °C and weigh after allowing to cool in a desiccator for 30 min. Assemble the flasks in series and immerse in the cooling mixture in separate baths (Figure 6). Connect to the liquid chlorine source. Collect about 225 ml of liquid chlorine in the first flask, using the method described in **A.3**, maintaining the cooling mixture at – 50 °C or lower. Close the container valve securely while the flasks are still connected and immersed in the cooling bath. Measure the volume in each flask after 5 min and record the temperature of the cooling baths. Disconnect from the chlorine source and insert the stoppers. Slowly vaporize the liquid chlorine as described in **A.5** and dispose of the chlorine vapour as described in **A.6** using 7 litres of 200 g/l sodium hydroxide solution. Allow vaporization to continue until 25 ml of the liquid are left in the first flask, as shown by the graduation mark.

NOTE The liquid chlorine boils at a temperature of about – 34 °C, and vaporizes at a rate of about 14 litres of gas per hour.

Replace the cooling baths and collect approximately a further 200 ml of liquid chlorine in the first flask and repeat the vaporization operation. Continue until the required amount of liquid chlorine has been collected and vaporized (about 1 kg).

When the final test portion has been taken, allow the residual liquid to vaporize completely and then disconnect the apparatus from the chlorine source.

Pass dry air through the flasks for about 6 min at a rate of about 250 ml/min as measured by the flowmeter (**F.3.1**). Dry the outside of each flask thoroughly with a clean cloth, place in a desiccator for 10 min and weigh.

Add together the volumes of liquid chlorine taken in the two sampling flasks, and calculate the total mass of sample evaporated from the liquid chlorine density curve (Figure 17).

F.5 Expression of results

The non-volatile residue, expressed as a percentage by mass of the sample of chlorine taken, is given by the formula:

$$\frac{M_1 \times 100}{M_2}$$

where

M_1 is the mass of residue (g)

M_2 is the mass of sample taken (g).

Appendix G Method for the determination of nitrogen trichloride content

NOTE There is no equivalent ISO method.

G.1 General

The method is suitable for measuring the nitrogen trichloride content in the range 1 mg/kg to 3 000 mg/kg of chlorine, without dilution.

G.2 Principle

Chlorine is vaporized and passed through concentrated hydrochloric acid solution to convert any nitrogen trichloride to ammonium chloride. The latter is determined colorimetrically as indophenol blue following reaction with sodium phenoxide/sodium hypochlorite reagent.

G.3 Reagents

The reagents used shall be of a recognized analytical grade. Water complying with the requirements of BS 3978, shall be used throughout.

G.3.1 *Ammonia-free air,* prepared by passing air through a Drechsel bottle containing hydrochloric acid solution (**G.3.3**) diluted with an equal volume of water.

G.3.2 *Phenol*

G.3.3 *Hydrochloric acid,* concentrated solution, 36 % (*m*/*m*), 11N, $\rho = 1.18$ g/ml, selected for low ammonia content. An absorbance for the “acid blank” of not greater than 0.03 in a 10 mm cell should be obtained, when measured as described in **G.5.1.1**.

G.3.4 *Acetone*

G.3.5 *Industrial methylated spirit,* 74° OP[2].

G.3.6 *Standard ammonium chloride solution A.* Dissolve 3.144 g of ammonium chloride in water and dilute to the mark in a 1 000 ml one-mark volumetric flask complying with the requirements of BS 1792.

1 ml of this solution is equivalent to 1 000 µg of ammonia.

G.3.7 *Standard ammonium chloride solution B.* Dilute 10 ml of solution A (**G.3.6**) to the mark in a 100 ml one-mark volumetric flask complying with the requirements of BS 1792.

1 ml of this solution is equivalent to 100 µg of ammonia.

G.3.8 *Sodium hypochlorite solution,* containing 0.6 % (*m*/*m*) of available chlorine.

G.3.9 *Sodium hydroxide,* 200 g/l solution.

G.3.10 *Sodium hydroxide,* 100 g/l solution.

G.3.11 *Sodium hydroxide,* 5 g/l solution.

G.3.12 *Sodium phenoxide solution.* Prepare as follows.

G.3.12.1 Dissolve 62.5 g of the phenol (**G.3.2**) in 18.5 ml of the acetone (**G.3.4**), dilute the solution to 100 ml with the industrial methylated spirit (**G.3.5**) and mix well. Store the solution in a refrigerator.

G.3.12.2 Dissolve 27 g of sodium hydroxide pellets in water, dilute the solution to 100 ml and mix well.

G.3.12.3 Prepare the sodium phenoxide solution by mixing 20 ml portions of each of the solutions (**G.3.12.1** and **G.3.12.2**) and diluting to 100 ml with water. Prepare only the minimum quantity and store in a refrigerator when not in use. Discard after 3 days.

G.3.13 *Sodium chloride solution.* Dissolve 34 g of sodium chloride in water and dilute to 1 000 ml.

G.3.14 *Starch iodide test papers*

G.3.15 *Glass wool*

G.3.16 *Silica gel* granules, approximate size 5 mm.

G.4 Apparatus

Ordinary laboratory apparatus and the following.

G.4.1 *Spectrophotometer,* capable of measuring at a wavelength of 625 mm and provided with 10 mm and 40 mm glass cells.

G.4.2 *pH meter*

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[2] The use of this material is governed by the Industrial Methylated Spirits Regulations 1952 (S.I. 1952 No. 2230).

G.4.3 *Magnetic stirrer*

G.4.4 *One-mark volumetric flasks,* 100 ml, complying with the requirements of BS 1792.

G.4.5 *Test tubes,* 150 × 25 stoppered type.

G.4.6 *Water bath*

G.4.7 *Two 100 ml sample flasks (Figure 7 A) with cooling baths,* as described in **A.3.1.1**.

G.4.8 *Bubblers* (protected from ultraviolet light).

G.4.9 *125* ml *Drechsel bottle,* containing glass wool.

G.4.10 *125* ml *Drechsel bottle,* containing silica gel.

G.4.11 *Flowmeter,* capable of measuring 500 ml of air per minute.

See Figure 19
and Figure 20

G.4.12 *Chlorine absorption apparatus,* as shown in Figure 9.

G.5 Procedure

G.5.1 *Preparation of calibration graph*

G.5.1.1 *0 to 100* µg *ammonia.* From a 10 ml burette, measure 0.25 ml, 0.5 ml and 1.0 ml portions of the standard ammonium chloride solution (**G.3.7**) (equivalent to 25 µg, 50 µg and 100 µg of NH_3) into 100 ml one-mark volumetric flasks. Dilute to the mark with the sodium chloride solution (**G.3.13**). Mix well and measure 15 ml of each solution into a stoppered test tube (**G.4.5**). Add 5 ml of the sodium phenoxide solution (**G.3.12**) followed by 5 ml of the sodium hypochlorite solution (**G.3.8**), mixing well after each addition.

Remove the stoppers and transfer the test tubes to the boiling water bath (**G.4.6**) for exactly 5 min in order to develop the colour, ensuring that the liquid level in the tubes is well below the boiling water level. Allow to cool to room temperature.

Carry out a blank determination using the sodium chloride solution (**G.3.13**) and use this solution in the reference cell when measuring the absorbance.

Measure the absorbance of the solution at a wavelength of approximately 625 nm using 40 mm glass cells in the spectrophotometer (**G.4.1**).

G.5.1.2 *100* µg *to 400* µg *ammonia.* Repeat the procedure described in **G.5.1.1** but using 1.0 ml, 2.0 ml and 4.0 ml of the ammonium chloride solution (**G.3.7**), giving solutions equivalent to 100 µg, 200 µg and 400 µg of ammonia.

Measure the absorbance of the solutions at a wavelength of approximately 625 nm using 10 mm glass cells.

Using the results from **G.5.1.1** and **G.5.1.2**, prepare a calibration graph of absorbance against micrograms of ammonia in 100 ml of solution.

G.5.2 *Preparation of test solutions.* Assemble two 100 ml sample flasks (**G.4.7**) as shown in Figure 6. Collect 20 ml to 100 ml of sample as described in **A.3** and note the temperature of the cooling baths. Add together the volumes of liquid chlorine taken in the two sample flasks and calculate the total mass, M_4, of sample from the liquid chlorine density graph (Figure 17).

Connect the outlet tube of the sample flask to a pair of the bubblers (**G.4.8**) which have been charged with 5.0 ml portions of the hydrochloric acid solution (**G.3.3**) (see Figure 19). Remove the cooling bath and allow the liquid chlorine to vaporize slowly over a period of about 30 min in a fume cupboard in the dark. Absorb the "waste" chlorine in 250 ml to 1 200 ml of the 200 g/l sodium hydroxide (**G.3.9**), depending upon the amount of sample taken (see **A.6** and Figure 9). Remove the cap from the inlet tube, quickly connect the latter to a source of the ammonia-free air (**G.3.1**) and purge the absorbers with the air at 500 ml/min to remove chlorine. When free from chlorine [check with the starch iodide papers (**G.3.14**)], transfer the contents of each bubbler into separate 100 ml beakers and bring the volumes up to about 50 ml with water. Into a third beaker, pipette 5.0 ml of the hydrochloric acid solution (**G.3.3**) and 45 ml of water to serve as a blank. Into a fourth beaker, pipette 5.0 ml of the hydrochloric acid solution (**G.3.3**) and 45 ml of water. Add to this beaker 0.5 ml of the standard ammonia solution (**G.3.7**) to serve as a standard reference solution for chlorine samples with low concentrations of nitrogen trichloride, or 2.0 ml of the standard ammonia solution (**G.3.7**) to serve as a standard reference solution for chlorine samples with high concentrations of nitrogen trichloride.

NOTE Under the test conditions specified, more than 90 % of nitrogen trichloride in the test portion should be absorbed in the first bubbler for levels up to 300 mg/kg. Higher levels may necessitate the use of a third bubbler charged with 5.0 ml of the hydrochloric acid solution (**G.3.3**).

G.5.3 *Colour development.* Using the pH meter (**G.4.2**), neutralize the acid solutions, first to pH 2.5 to 3.0 with the sodium hydroxide solution (**G.3.10**) and then to pH 6.0 to 7.0 with the sodium hydroxide solution (**G.3.11**), mixing the solutions by means of the magnetic stirrer (**G.4.3**). Dilute the neutralized solutions to exactly 100 ml and mix well to give stock solutions of the sample, the acid blank and the standard reference solution. Transfer a 15 ml portion of each of these solutions into the stoppered test tubes (**G.4.5**) and add 5 ml of the sodium phenoxide solution (**G.3.12**) followed by 5 ml of the sodium hypochlorite solution (**G.3.8**), mixing well after each addition. Remove the stoppers and transfer the test tubes to the boiling water bath (**G.4.6**) for exactly 5 min to develop the colour, ensuring that the liquid level in the test tubes is well below the boiling water level. Cool to room temperature and measure the absorbance of the sample solutions on the spectrophotometer with the acid blank solution in the reference cell. Use the appropriate cell size and the conditions described in **G.5.1**.

If an absorbance exceeds that of the highest calibration standard, discard the test and repeat with a smaller aliquot portion from the sample stock solution after diluting this aliquot portion to 15 ml with the stock solution of the acid blank.

G.5.4 *Spectrophotometric measurements.* From the previously prepared calibration graph, read off the amount of ammonia in each of the sample solutions and in the standard reference solution(s). Make due allowance for any change to the normal 15 ml aliquot portion (**G.5.3**) taken for the colour development.

G.6 Expression of results

Nitrogen trichloride content, expressed in milligrams per kilogram of chlorine, is given by the formula:

$$\frac{M_1 \times M_2}{M_3 \times M_4} \times 7.08$$

where

M_1 is the sum of the masses of ammonia in sample solutions (μg)

M_2 is the mass of ammonia added to appropriate standard reference solution (μg)

M_3 is the mass of ammonia obtained for appropriate standard reference solution (μg)

M_4 is the mass of the sample (g)

7.08 is the conversion factor of ammonia to nitrogen trichloride.

G.7 Precautions when sampling liquid chlorine for nitrogen trichloride determination

G.7.1 Nitrogen trichloride can be decomposed by exposure to light. All parts of the apparatus in which the sample may be so exposed before or during contact with hydrochloric acid should therefore be suitably masked (black plastics self-adhesive tape is recommended). Ensure also, during sample collection, that sources of ultraviolet light, e.g. fluorescent tube lighting, are turned off.

G.7.2 Nitrogen trichloride decomposes rapidly in contact with certain metal surfaces. Liquid chlorine transfer lines, dip pipes etc. should consequently be purged thoroughly before sampling to ensure that truly representative samples of liquid are obtained. Samples taken in cylinders should be tested immediately after filling to ensure a satisfactory result.

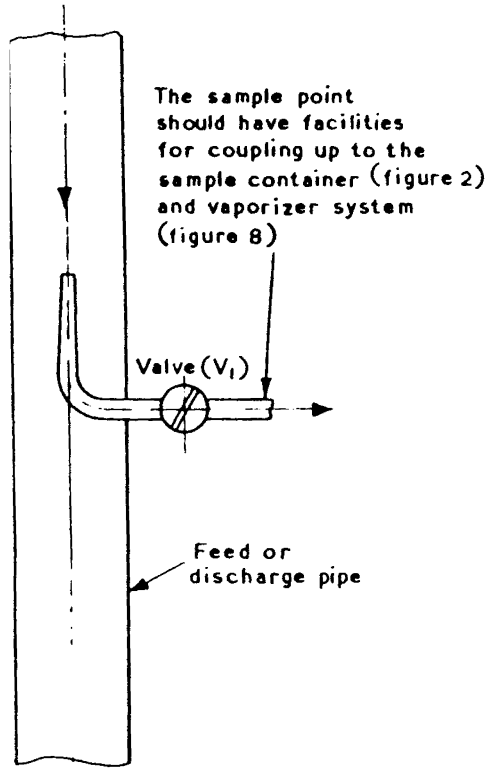


Figure 1 — Diagram of sample point from a pipe containing a flowing stream of liquid chlorine

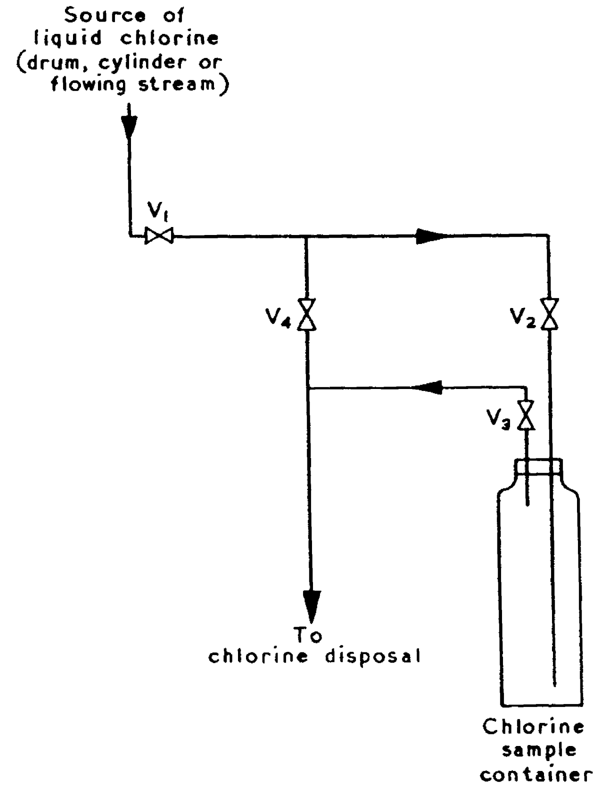


Figure 2 — Sampling into pressurized sample containers

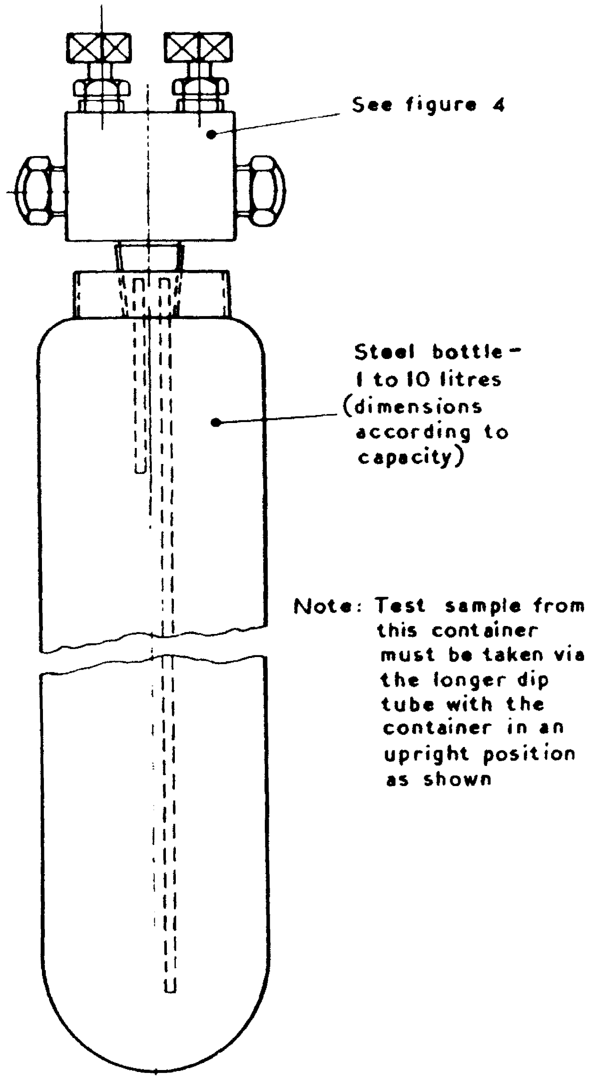


Figure 3 — Liquid chlorine sample container

Dimensions in millimetres

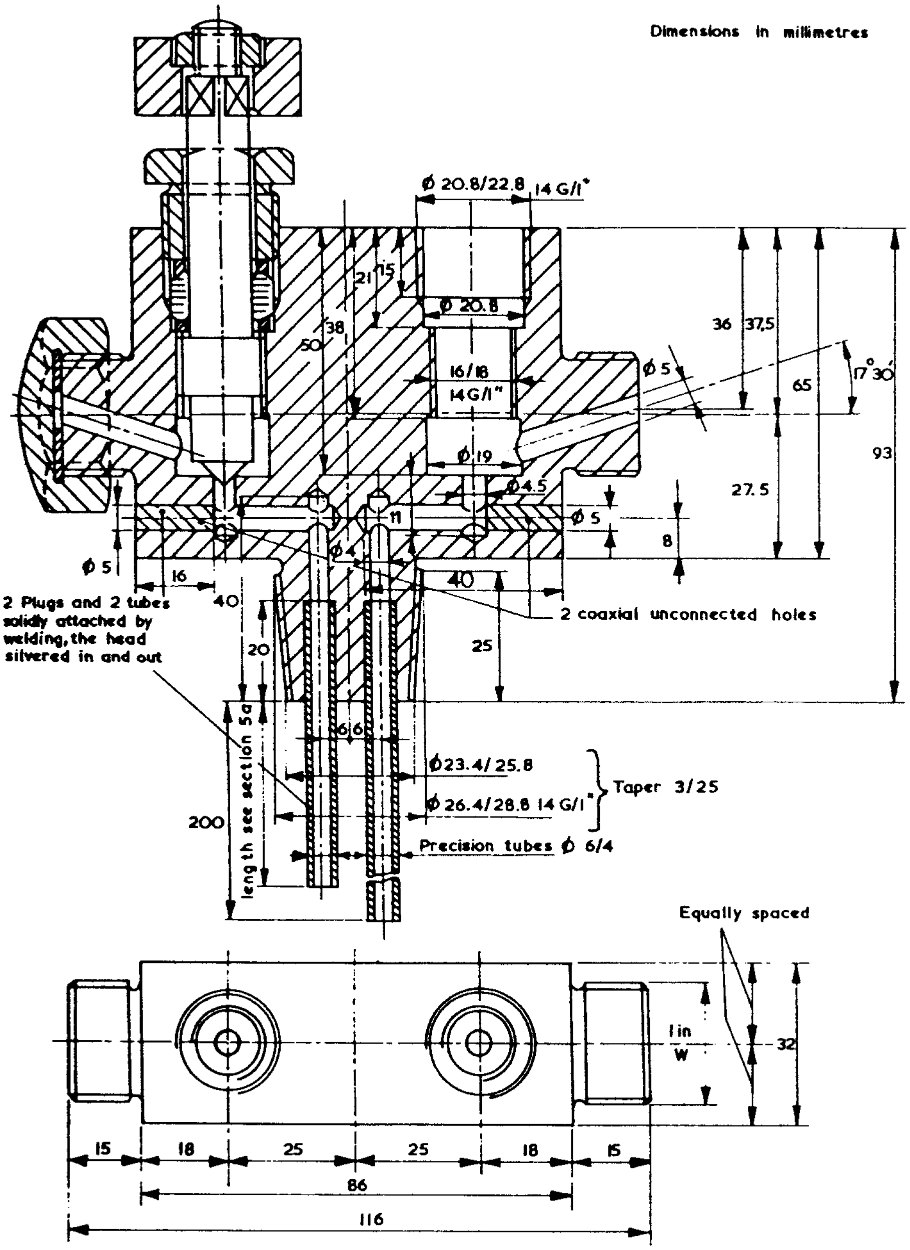


Figure 4 — Head of liquid chlorine sample container

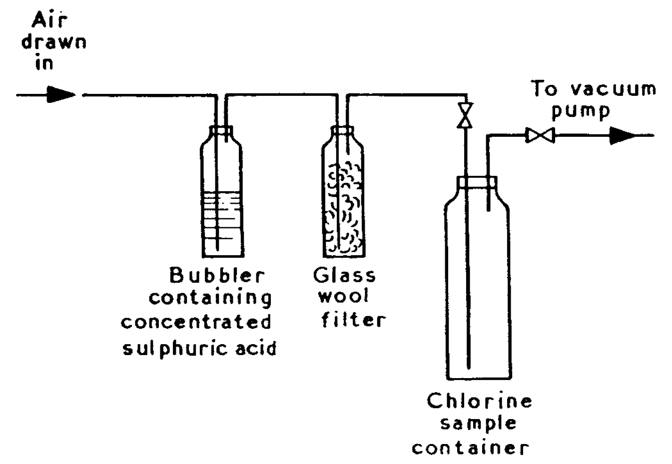


Figure 5 — Checking of chlorine sample container before taking the sample

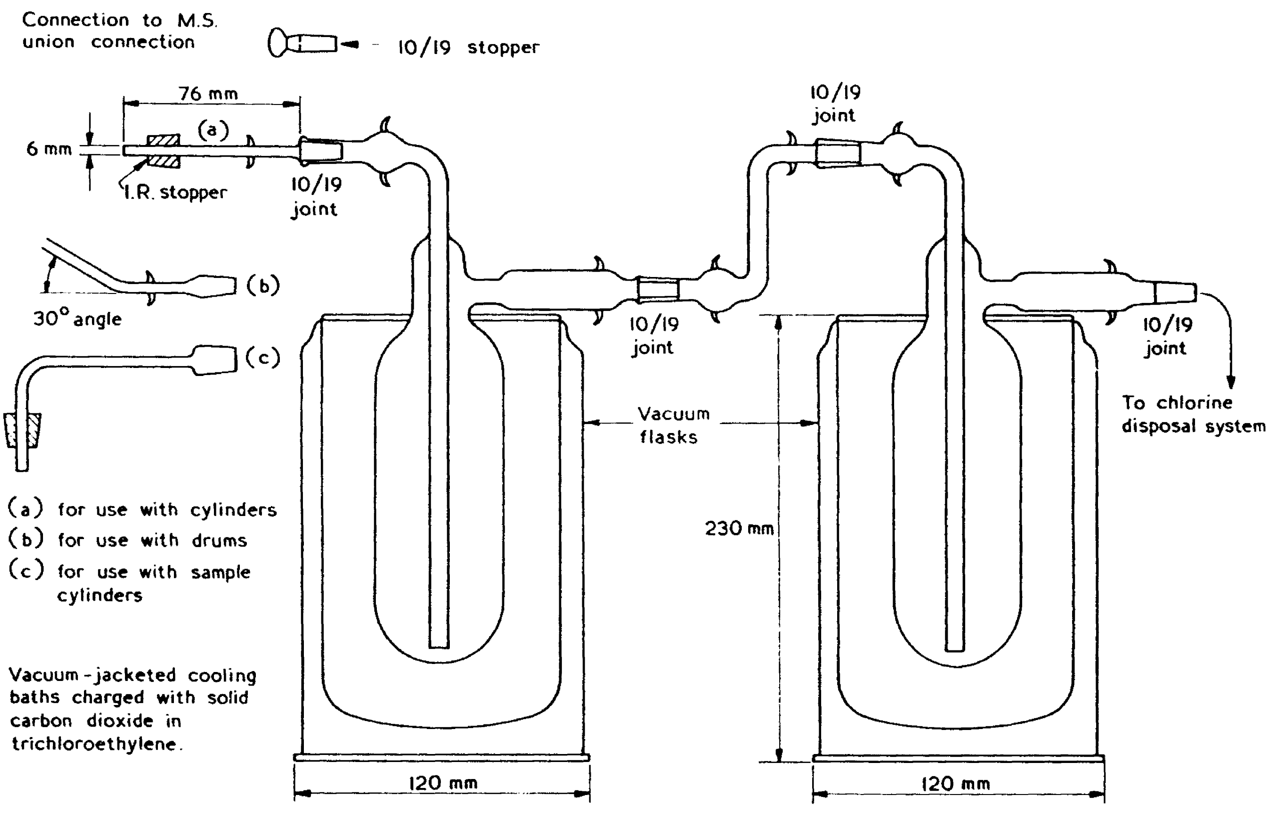
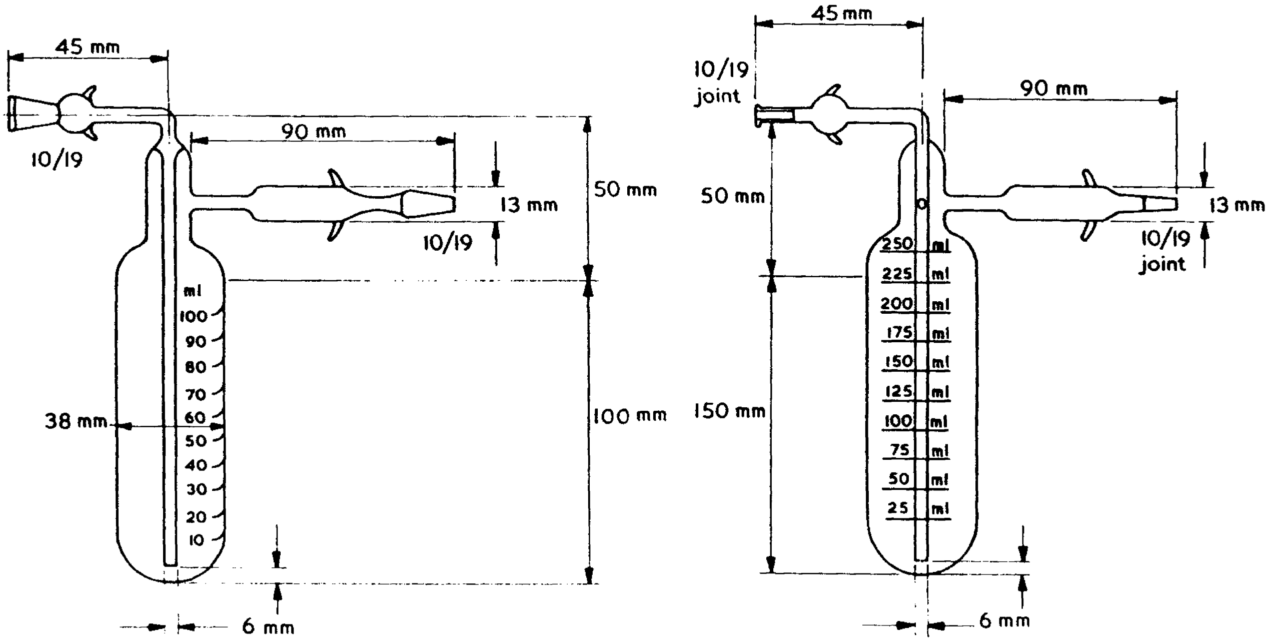


Figure 6 — Sampling into non-pressurized sample containers



A. Sample flask for nitrogen trichloride determination

B. Sample flask for residue on evaporation determination

Figure 7 — Non-pressurized sample containers

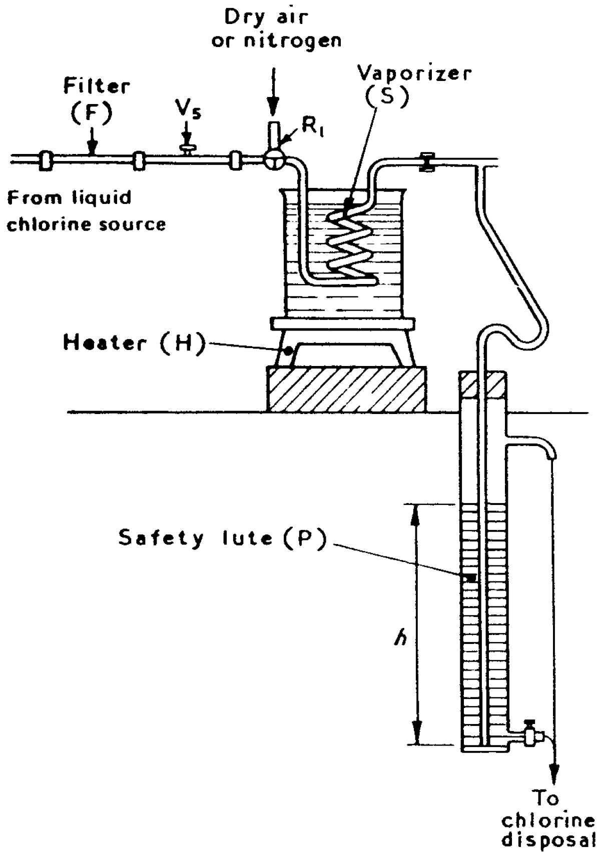


Figure 8 — Vaporization of a sample from a pressurized source

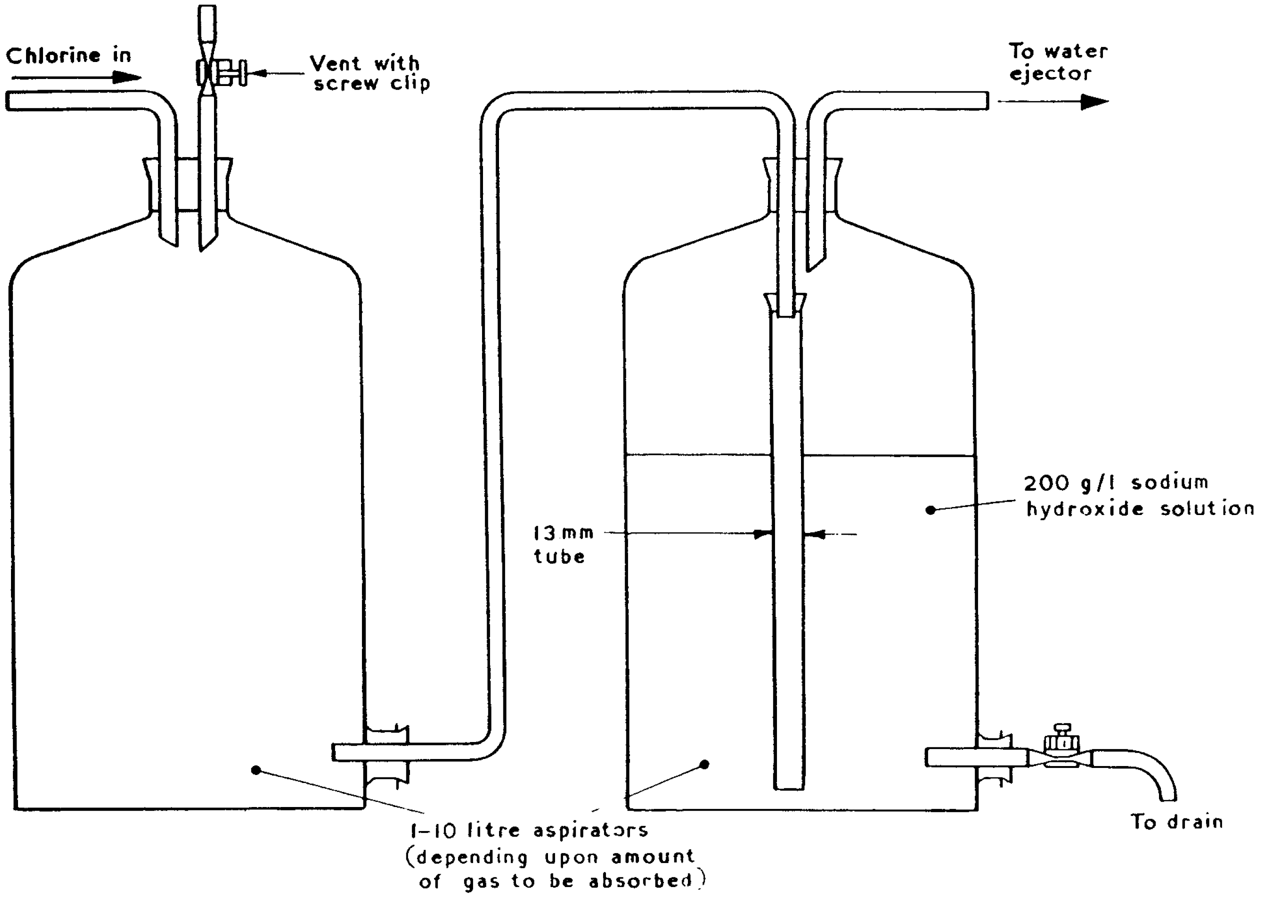


Figure 9 — Chlorine absorption apparatus

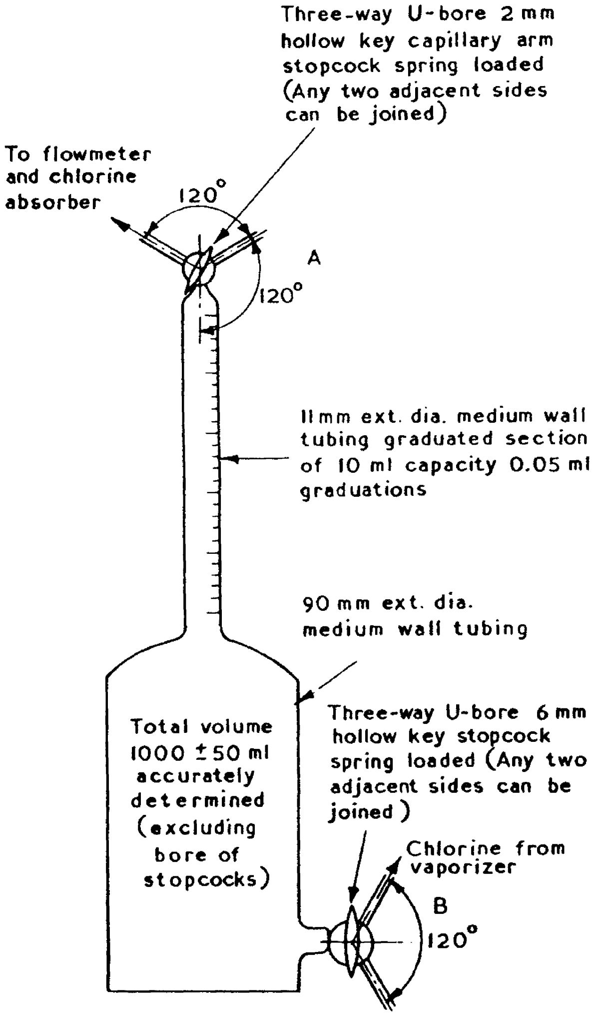


Figure 10 — Volumetric flask for determining chlorine content

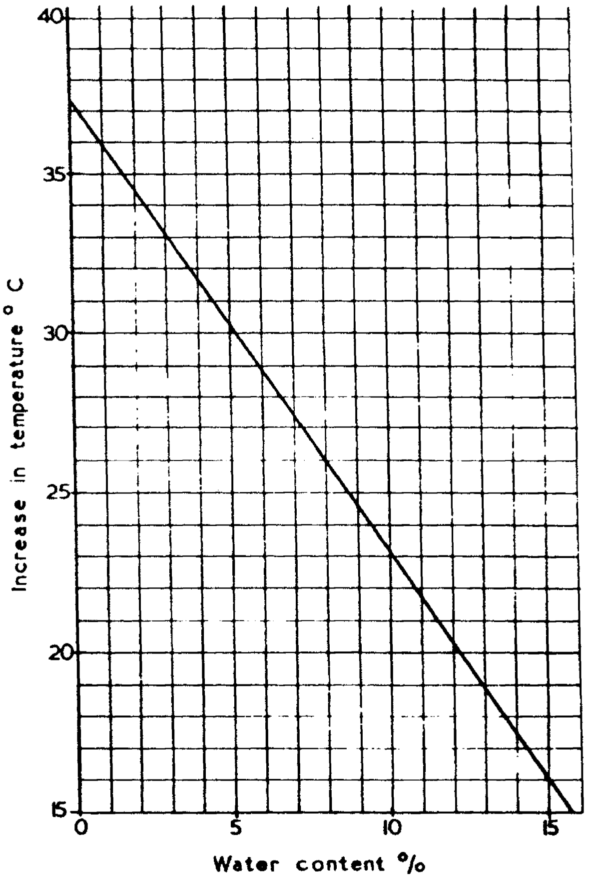


Figure 11 — Calibration graph giving the water content of the magnesium perchlorate as a function of the increase in temperature resulting from the heat of solution under the conditions of C.10

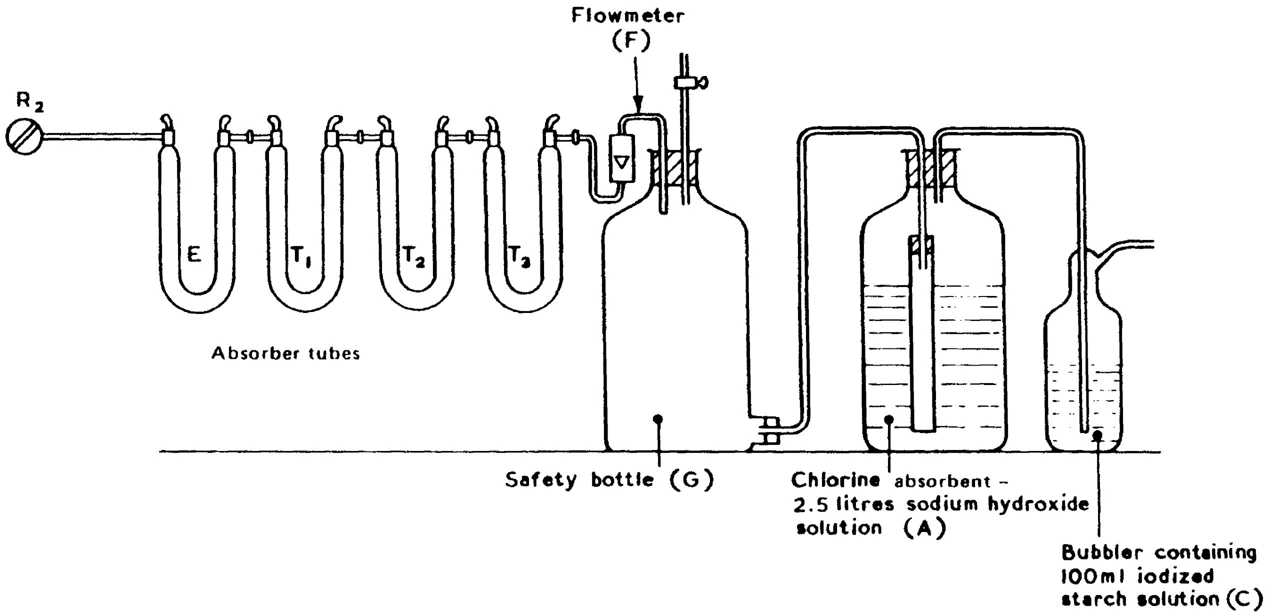


Figure 12 — Determination of water content: gravimetric method

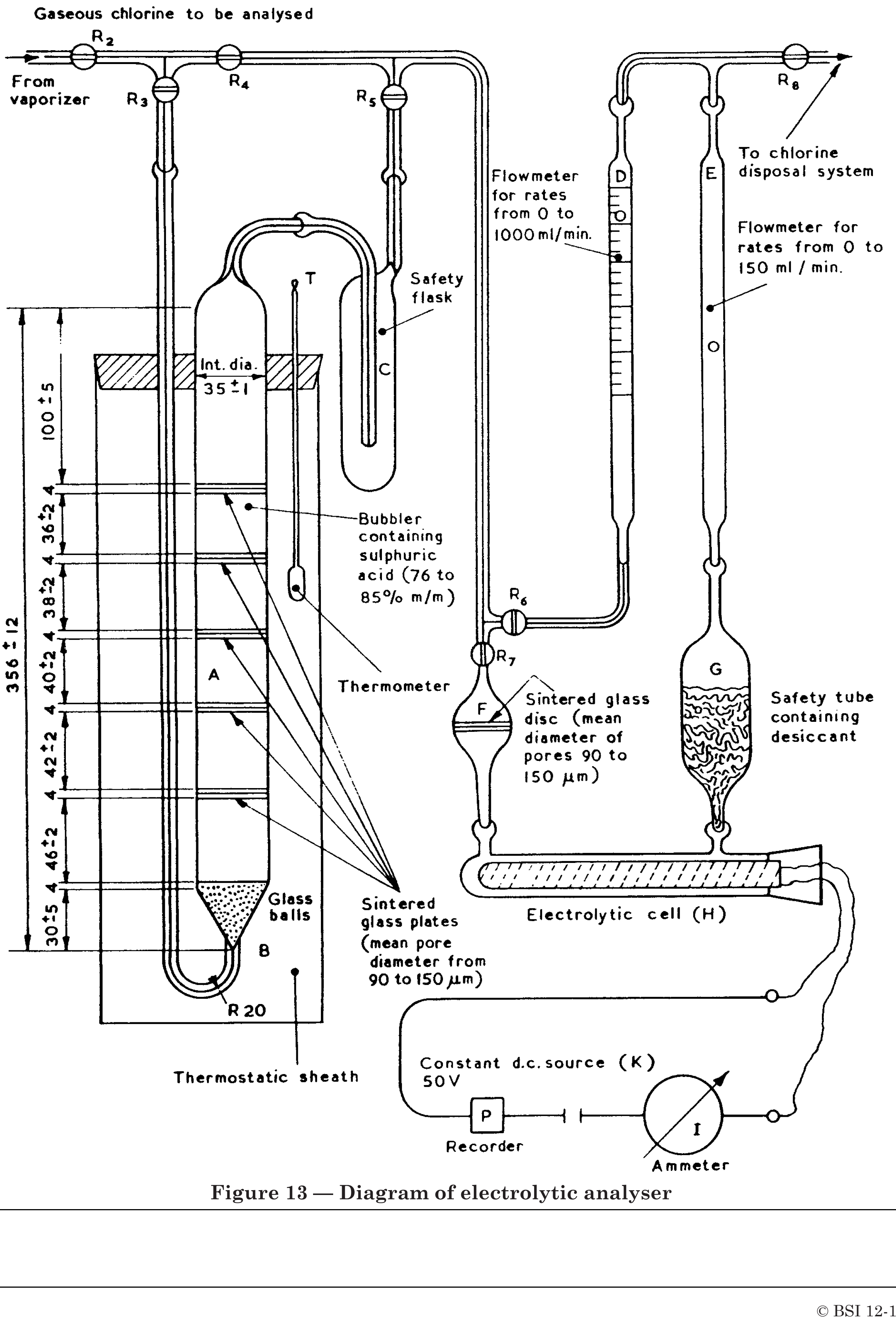


Figure 13 — Diagram of electrolytic analyser

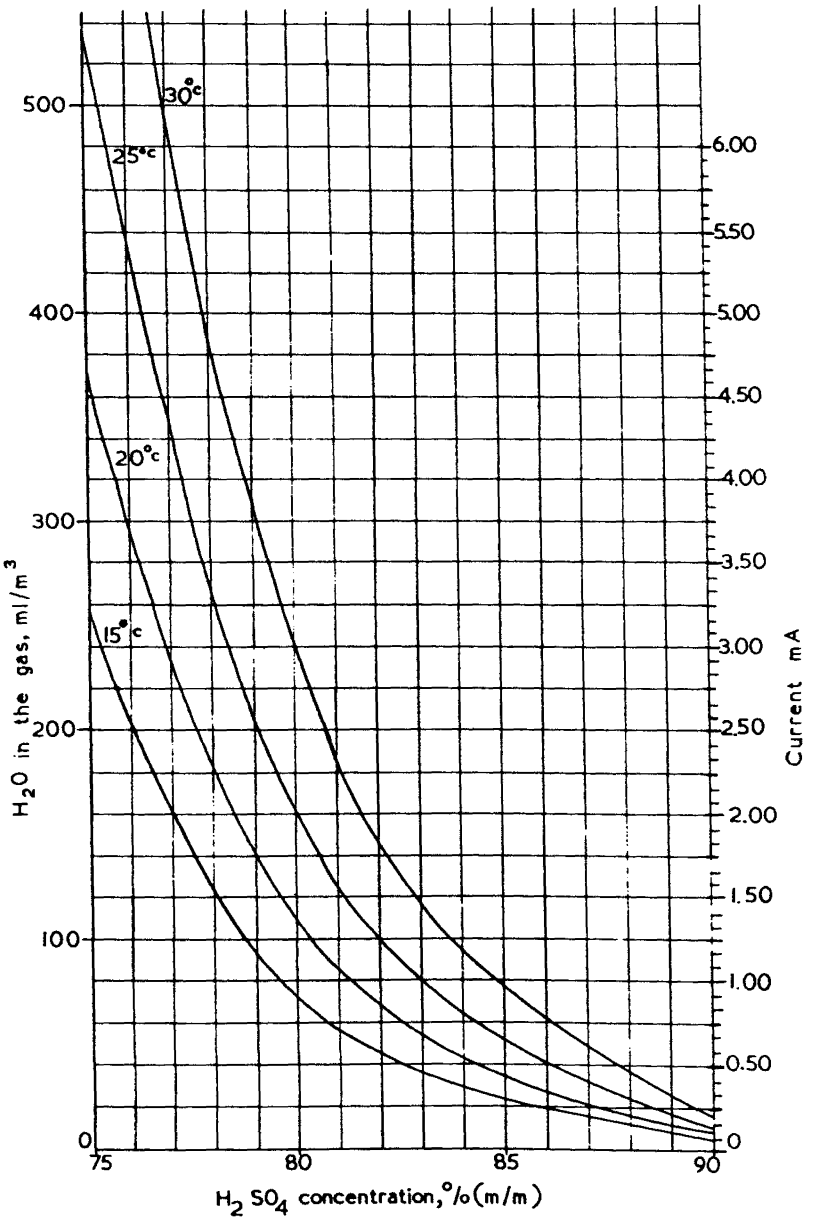


Figure 14 — Equilibrium diagram showing moisture content of chlorine after bubbling in sulphuric acid as a function of acid concentration and temperature

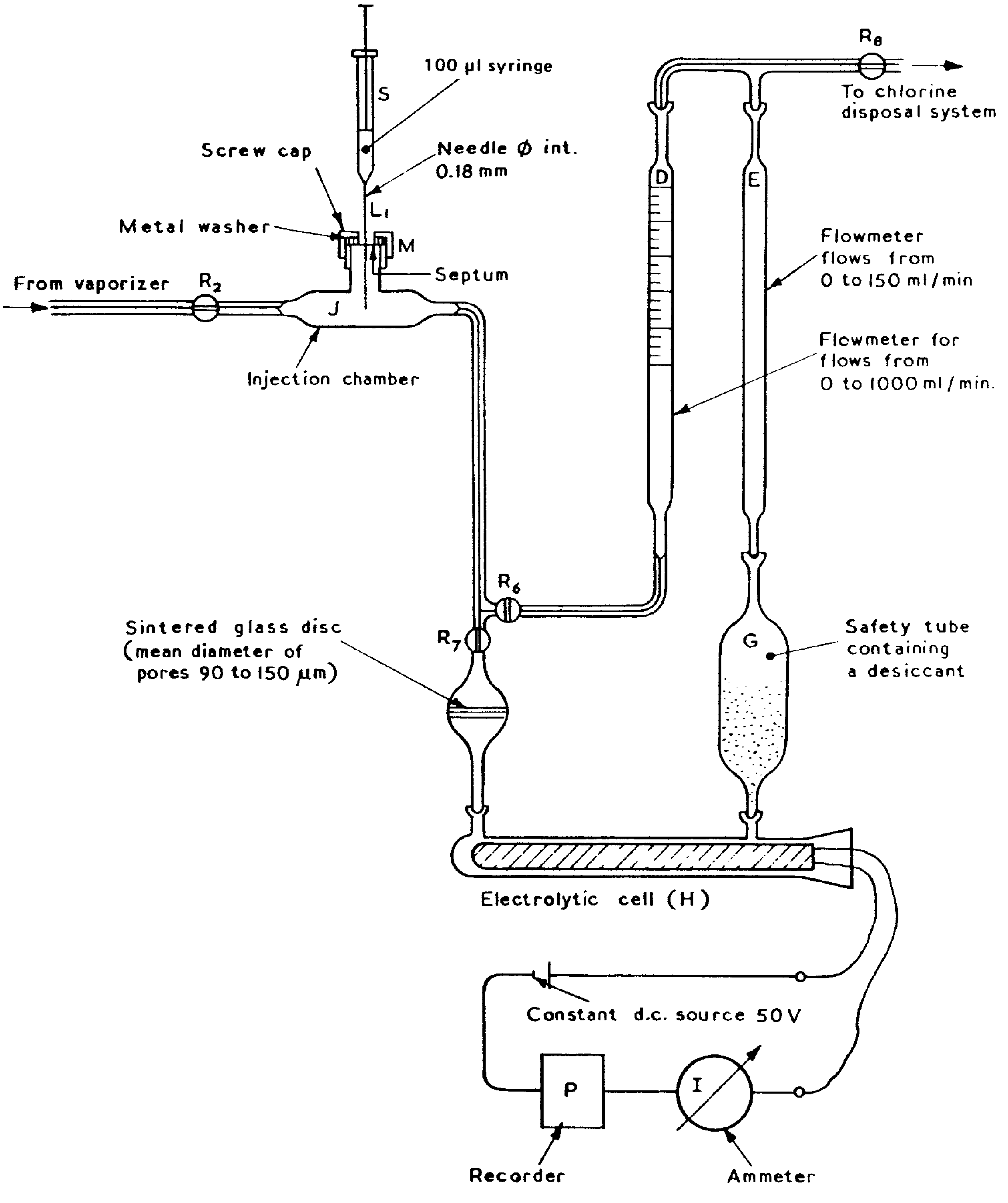


Figure 15 — Diagram of an electrolytic analyser and the calibration device

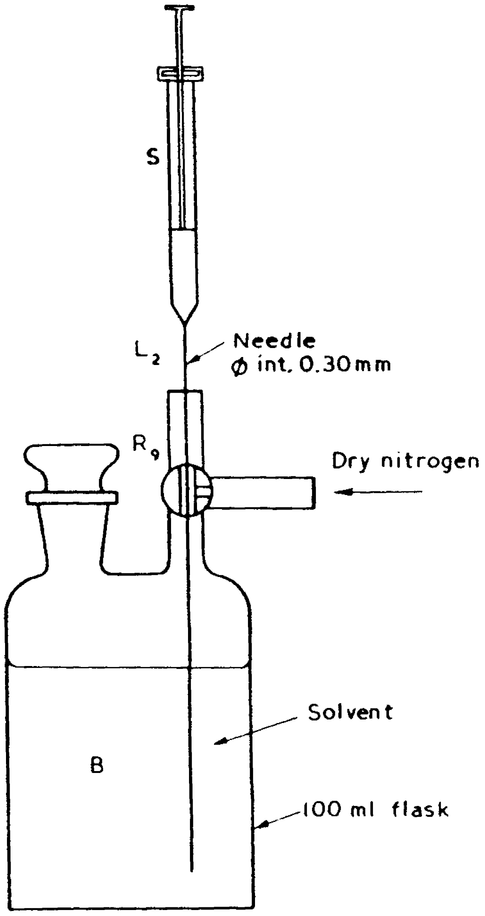


Figure 16 — Device for drawing off solvent

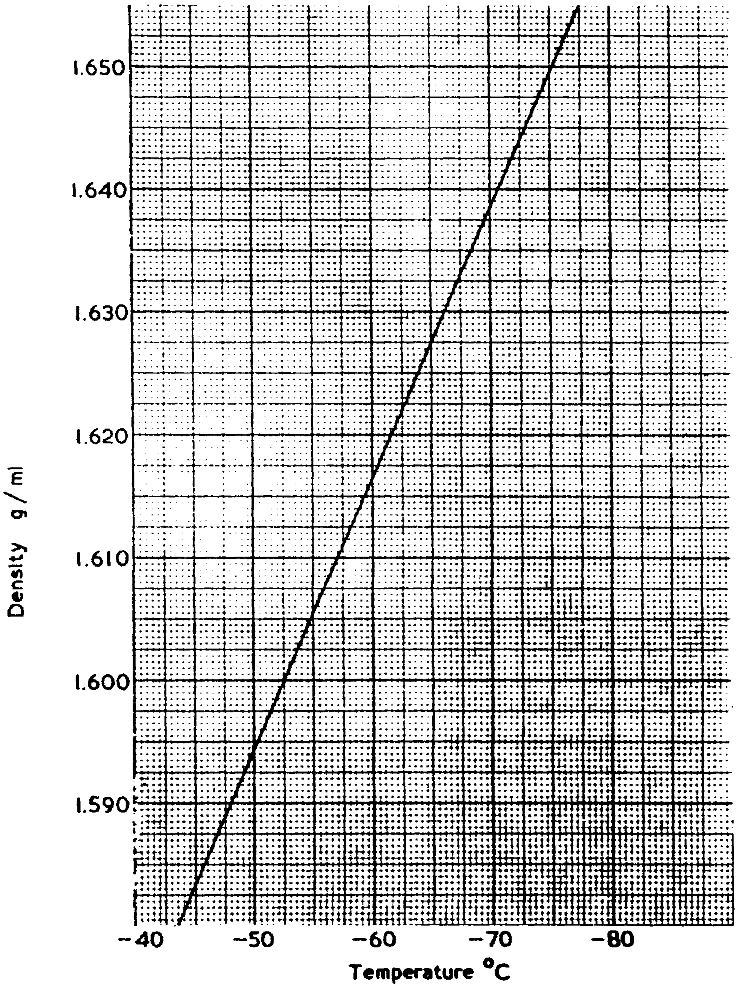


Figure 17 — Liquid chlorine. Variation of density with temperature

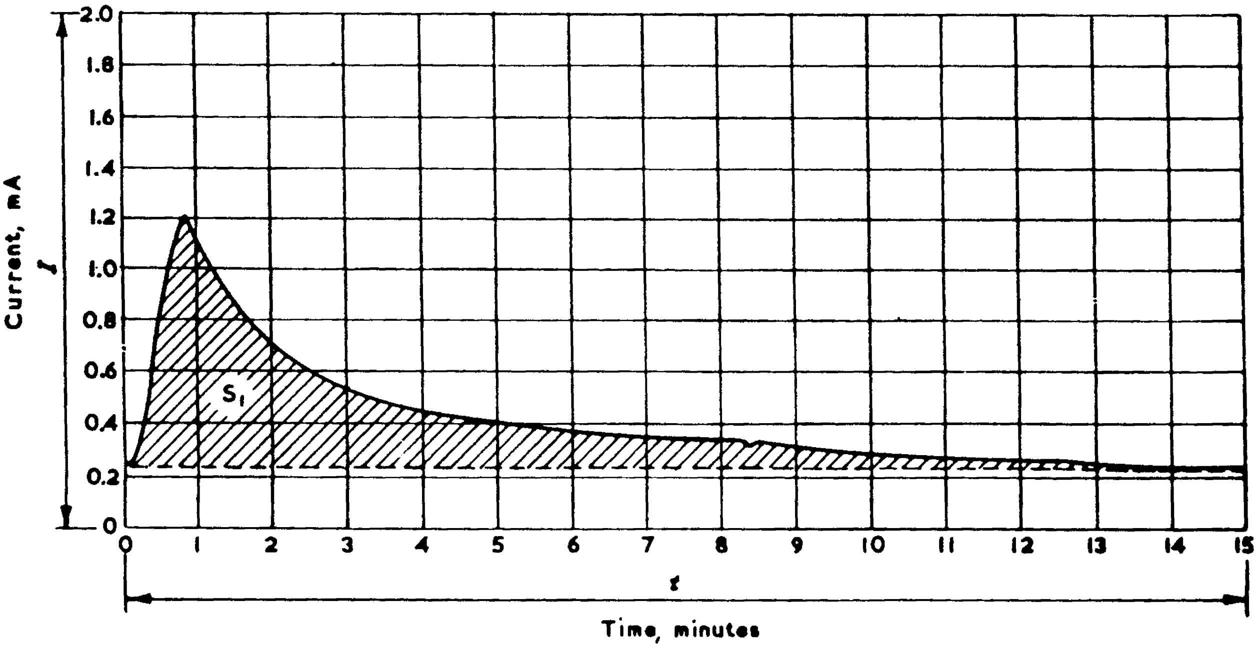


Figure 18 — Example of recorder chart

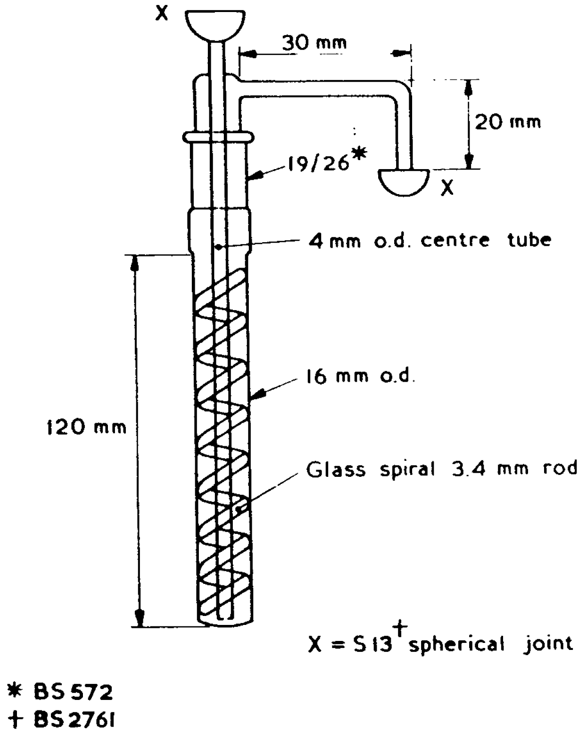
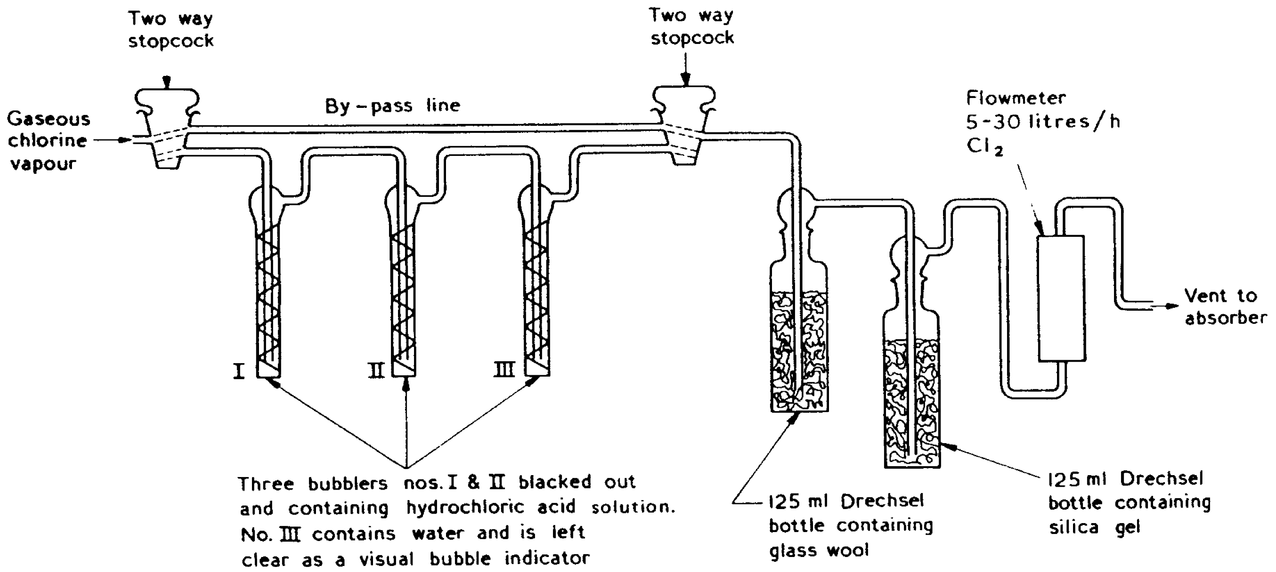


Figure 19 — Bubbler for determination of nitrogen trichloride



NOTE All parts of the apparatus prior to the absorbers to be blacked out

Figure 20 — Apparatus for determination of nitrogen trichloride content

Publications referred to

BS 349, *Identification of contents of industrial gas containers.*

BS 401, *Steel cylinders for the storage and transport of "liquefiable" gases.*

BS 572, *Interchangeable conical ground glass joints.*

BS 604, *Graduated measuring cylinders.*

BS 1704, *General purpose thermometers.*

BS 1792, *One-mark volumetric flasks.*

BS 2511, *Methods for the determination of water (Karl Fischer method).*

BS 2761, *Spherical ground glass joints.*

BS 3978, *Water for laboratory use.*

ISO/R 1552, *Liquid chlorine for industrial use — Method of sampling (for determining only the volumetric chlorine content).*

ISO 2120, *Liquid chlorine for industrial use — Determination of the content of chlorine by volume in the vaporized product.*

ISO 2121, *Liquid chlorine for industrial use — Determination of water content — Gravimetric method.*

ISO 2202 and Addendum 1, *Liquid chlorine for industrial use — Determination of water content using an electrolytic analyser.*

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