

Methods of test for

Potassium hydroxide

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The 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:

- Asbestos Cement Manufacturers Association
- British Man-made Fibres Federation
- British Textile Employers' Association
- Fabric Care Research Association
- Society of Glass Technology

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Foreword

This British Standard, prepared under the direction of the Chemicals Standards Committee, comprises methods of test for potassium hydroxide in solid form and in aqueous solution. It provides a full range of tests for use in conjunction with BS 5633, which specifies potassium hydroxide for use in alkaline cells. Not all of these tests may be necessary when testing potassium hydroxide for other industrial uses (in such cases the methods may be used selectively).

The opportunity has been taken, where appropriate, to incorporate substantially the technical content of International Standards from the series of methods of test for potassium hydroxide for industrial use which has been prepared, with the active participation of the United Kingdom, by Sub-committee 5 of Technical Committee 47, Chemistry, of the International Organization for Standardization (ISO). The relationship between the appropriate British Standard methods and the International Standards is shown in the table below.

The method of ISO 2466 has been modified by the introduction of two sample solutions, one a solution of the sample corresponding to solution A in ISO 2466 and the other an acidified solution of the sample, designated solution B. A third solution, designated C, is a blank for the acid used in the preparation of solution B. If it is necessary to determine all the trace metals, the use of solution B results in considerable saving of time.

The procedure used for the determination of arsenic, which is the same as that described in BS 4404, is technically similar to the method given in ISO 2590.

Atomic absorption methods are described for the determinations of calcium, zinc and lead. The flame emission photometric method used for the determination of sodium is similar in principle to that described in ISO 1550 but, in accordance with United Kingdom comments not accepted by the ISO committee, does not restrict the fuel for the atomizer-burner of the flame spectrophotometer to a butane/air mixture.

Other International Standards in the series of methods of test for potassium hydroxide for industrial use will be published as addenda to this British Standard, subject to their approval by the United Kingdom.

There are at present no ISO methods for the determination of the contents of nitrate, cyanide, zinc, copper, lead and nickel in potassium hydroxide.

BS 5634: Preparation/ Determination of	Corresponding International Standard
sample solutions	ISO 2466, " <i>Potassium hydroxide for industrial use — Sampling — Test sample — Preparation of the main solution for carrying out certain determinations</i> "
total hydroxide content	ISO 990, " <i>Potassium hydroxide for industrial use — Method of assay</i> "
carbonate content	ISO 2900, " <i>Potassium hydroxide for industrial use — Determination of carbon dioxide content — Titrimetric method</i> "
chloride content	ISO 3177, " <i>Potassium hydroxide for industrial use — Determination of chlorides content — Photometric method</i> "
content of sulphur compounds	ISO 3194, " <i>Potassium hydroxide for industrial use — Determination of sulphur compounds — Method by reduction and titrimetry</i> "
silica content	ISO 995, " <i>Potassium hydroxide for industrial use — Determination of silica content — Reduced molybdosilicate photometric method</i> "

BS 5634: Preparation/ Determination of	Corresponding International Standard
calcium content	ISO 3698, " <i>Potassium hydroxide for industrial use — Determination of calcium and magnesium contents — Flame atomic absorption method</i> "
iron content	ISO 994, " <i>Potassium hydroxide for industrial use — Determination of iron content — 1,10-Phenanthroline photometric method</i> "

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Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 26, 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.

Section 1. General

1 Scope

This British Standard specifies methods for sampling and testing potassium hydroxide in solid form and in aqueous solution.

2 References

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

3 Preparation of sample solution

3.1 Principle. Three solutions are prepared, solution A which is a solution of the sample in water, solution B which is an acidified solution of the sample in water and solution C which is a blank for the acid used in preparing solution B.

NOTE The use of these bulk sample solutions serves to reduce sampling errors. In the case of solution B, acidification ensures dissolution of metallic impurities and allows more uniform sampling for the determination of metallic impurities.

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

3.2.1 Hydrochloric acid, approximately 5N solution.

3.2.2 Methyl orange indicator solution, 0.4 g/l, prepared as described in BS 4123.

3.3 Apparatus. Ordinary laboratory apparatus is required.

3.4 Procedure

3.4.1 Preliminary treatment of sample. Protect the laboratory sample from the atmosphere and handle it in such a way that no appreciable absorption of moisture or carbon dioxide or reaction with silica can occur.

The maximum particle size of solid test portions shall not exceed about 6 mm. If crushing is necessary, carry it out as quickly as possible, in as inert an atmosphere as possible, preferably in an unventilated glove box containing evenly-distributed shallow dishes of phosphorus (V) oxide and similar dishes of potassium hydroxide pellets to remove water vapour and carbon dioxide, respectively. These absorbents should be left in the glove box for at least 1 h before it is used.

3.4.2 Preparation of solution A. Weigh, accurately, 100 ± 1 g of the solid sample or 200 ± 2 g of the liquid sample into an alkali-resistant container fitted with a lid. If the sample is solid, dissolve it in 250 ml of freshly boiled and cooled water in an alkali-resistant beaker and cool. Transfer the solution, or the original sample if liquid, to a 500 ml alkali-resistant graduated cylinder, dilute to the mark with water, mix and transfer immediately to an airtight, alkali-resistant plastics bottle. Label as "Solution A".

3.4.3 Preparation of solution B. Weigh 10.0 ± 0.1 g of the solid sample, or 20.0 ± 0.2 g of the liquid sample, into a 250 ml beaker. Add 50 ml of water, swirl to dissolve or mix, and titrate with the hydrochloric acid solution (3.2.1) using the methyl orange solution (3.2.2) as indicator. Let the titration be X ml. Discard the solution.

Weigh, accurately, 100 ± 1 g of the solid sample or 200 ± 2 g of the liquid sample into a 1 000 ml beaker. Add 200 ml of water and swirl to dissolve or mix. From a measuring cylinder cautiously add $(10X + 5)$ ml of the hydrochloric acid solution (3.2.1) with continuous stirring. Cool the contents of the beaker to ambient temperature, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix. Label as "Solution B".

3.4.4 Preparation of solution C.

Evaporate $(10X + 5)$ ml (see 3.4.3) of the hydrochloric acid solution (3.2.1) to 5 ml in a 1 000 ml beaker, taking care to avoid contamination. Transfer the residual solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix. Label as "Solution C".

Section 2. Methods of test

4 Determination of total hydroxide content

4.1 Field of application. The method is applicable to all commercial products, both solid and liquid.

4.2 Principle. The total alkalinity content is determined by titration with hydrochloric acid solution using methyl orange as indicator and a correction is made for the carbonate content, determined by the method of test specified in clause 5, to give total hydroxide content.

4.3 Reagents. The reagents used shall be of recognized analytical quality. Water complying with the requirements of BS 3978, freshly boiled to free it from carbon dioxide, shall be used throughout.

4.3.1 Hydrochloric acid, 1N standard volumetric solution.

4.3.2 Methyl orange indicator solution, 0.4 g/l, prepared as described in BS 4123.

4.4 Apparatus. Ordinary laboratory apparatus and the following are required.

4.4.1 Burette, 50 ml capacity, complying with the requirements for class A of BS 846.

4.5 Procedure. Weigh, to the nearest 0.01 g, 25 g of the solid sample or 50 g of the liquid sample. Dissolve in or mix with 200 ml of water in a 400 ml beaker. Cool and transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix. Pipette 50.0 ml of this solution into a 500 ml conical flask. Add 80 ml of water and five drops of the methyl orange solution (4.3.2) and titrate with the hydrochloric solution (4.3.1) until the colour changes from yellow to orange.

4.6 Expression of results. The total hydroxide content, expressed as the percentage by mass of potassium hydroxide (KOH), is given by the following formula:

$$\frac{56.1 \times V}{m} - 0.8124$$

where

V is the volume of the hydrochloric acid solution (4.3.1) used in the determination of total alkali (in ml)

m is the mass of the test portion (in g)

A is the carbonate content of the sample, expressed as the percentage by mass of potassium carbonate (K_2CO_3) (see clause 5)

5 Determination of carbonate content

5.1 Field of application. The method is applicable to products having carbonate contents, expressed as potassium carbonate (K_2CO_3), greater than 0.02 % m/m .

5.2 Principle. Carbon dioxide is released by acidifying and heating the test solution. The released carbon dioxide is entrained in a current of nitrogen or air and absorbed in standard barium hydroxide solution. The excess barium hydroxide is titrated with a standard volumetric solution of hydrochloric acid using thymolphthalein as indicator.

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

5.3.1 Hydrochloric acid, approximately 5N solution.

5.3.2 Hydrochloric acid, 0.1N standard volumetric solution.

5.3.3 Barium hydroxide, approximately 0.1N solution.

Weigh 15 ± 0.1 g of barium hydroxide octahydrate, $[Ba(OH)_2 \cdot 8H_2O]$, dissolve in water, dilute to 1 000 ml and mix. Allow precipitated barium carbonate to settle out before use.

5.3.4 Methyl orange indicator solution, 0.4 g/l, prepared as described in BS 4123.

5.3.5 Thymolphthalein indicator solution, 2 g/l, prepared as described in BS 4123.

5.3.6 Nitrogen or air, free from carbon dioxide.

5.4 Apparatus. Ordinary laboratory apparatus and the following are required.

5.4.1 Apparatus for the release, absorption and titration of carbon dioxide. A typical apparatus, shown in Figure 1, comprises

- A flask, 500 ml capacity
- B dropping funnel, 100 ml capacity
- C_1 and C_2 Drechsel bottles, containing 20 % m/m sodium hydroxide solution
- C_3 Drechsel bottle, containing saturated barium hydroxide solution
- D spiral condenser
- E absorption vessel
- F absorption coil, made from glass tubing of diameter 7 mm to 8 mm and consisting of five or six turns of diameter 55 mm to 60 mm
- G burette, 50 ml capacity, complying with the requirements for class A of BS 846
- H stopcock
- J inlet for nitrogen or air (free from carbon dioxide)
- K outlet for nitrogen or air (free from carbon dioxide)
- L mercury lute fitted with guard tube containing activated charcoal

5.5 Procedure

5.5.1 Test portion. Measure out a volume of the solution A (3.4.2) containing not more than 25 g of potassium hydroxide or 150 mg of potassium carbonate.

5.5.2 Blank test. Subsequent to the determination, carry out a blank test following the procedure specified in 5.5.3 but omitting the test portion.

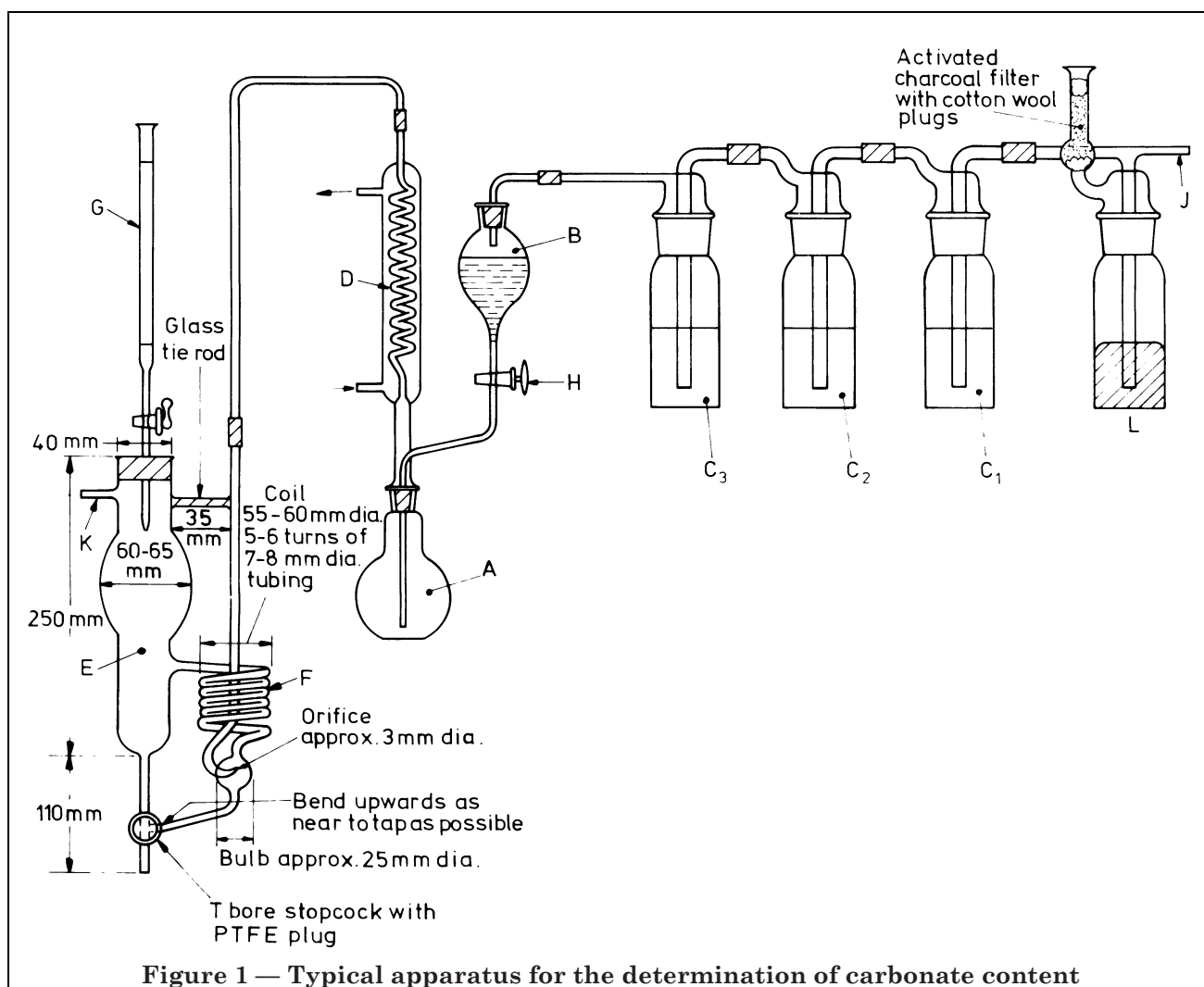


Figure 1 — Typical apparatus for the determination of carbonate content

5.5.3 Determination. Pass the nitrogen or the air (5.3.6) through the apparatus at a rate of about 5 bubbles per second for 10 min. Stop the current of gas and introduce the test portions and reagents into the apparatus as follows:

- into the dropping funnel (B) about 100 ml of the hydrochloric acid solution (5.3.1);
- into the flask (A) the test portion (5.5.1), diluted to 150 ml with water, and three drops of the methyl orange solution (5.3.4);
- into the absorption vessel (E) 50.00 ml of the barium hydroxide solution (5.3.3) and 10 drops of the thymolphthalein solution (5.3.5).

Close the apparatus, start the flow of water into the jacket of the condenser (D) and carefully allow the acid in the dropping funnel (B) to run into the flask (A). Check that the solution is now acid.

Pass a current of the gas (5.3.6), controlled to 2 bubbles per second for 10 min and then, without interrupting the flow, heat the contents of the flask (A) just to boiling and maintain at this temperature for 20 min. Stop heating, increase the gas flow to 5 bubbles per second and titrate the excess of the barium hydroxide solution contained in the vessel (E) with the standard volumetric hydrochloric acid solution (5.3.2), using the burette (G), until the blue colour of the indicator just changes to colourless.

5.6 Expression of results. The carbonate content, expressed as a percentage by mass of potassium carbonate (K_2CO_3), is given by the following formula:

$$(V_0 - V_1) \times \frac{500}{V_2} \times \frac{100}{m_0} \times 0.0069 = \frac{345 (V_0 - V_1)}{V_2 \times m_0}$$

where

V_0 is the volume of the standard volumetric hydrochloric acid solution (5.3.2) used for the blank (in ml)

V_1 is the volume of the standard volumetric hydrochloric acid solution (5.3.2) used for the determination (in ml)

V_2 is the aliquot portion of solution A taken for the test (in ml)

m_0 is the mass of sample used in the preparation of solution A (in g)

6 Determination of sodium content

6.1 Field of application. The method is applicable to products having sodium contents, expressed as sodium hydroxide (NaOH), in the range 0.2 % to 2 % *m/m* for liquid products and 0.4 % to 4 % *m/m* for solid products.

6.2 Principle. The sample solution is neutralized with hydrochloric acid and acidified by the addition of a small excess. The sodium content is then determined using either a flame photometer with a sodium filter or a flame spectrophotometer set at a wavelength of about 589 nm.

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

6.3.1 Hydrochloric acid, approximately 1N solution.

6.3.2 Methyl orange indicator solution, 0.4 g/l, prepared as described in BS 4123.

6.3.3 Potassium hydrogen carbonate, 89 g/l solution. Store in a plastics container.

6.3.4 Sodium chloride, standard solution, corresponding to 2 000 g of sodium hydroxide per litre.

Dissolve 2.925 g of sodium chloride, previously dried at a temperature of 500 °C, in water and dilute to the mark in a 1 000 ml one-mark volumetric flask. Mix.

1 ml of this solution contains the equivalent of 2 mg of NaOH.

6.4 Apparatus. Ordinary laboratory apparatus and the following are required.

6.4.1 Flame photometer, fitted with a sodium filter, with appropriate gas supplies, or

6.4.2 Flame spectrophotometer, with appropriate gas supplies.

6.5 Procedure

6.5.1 Test portion. Using a pipette, transfer 10.0 ml of the solution A (3.4.2) into a 100 ml one-mark volumetric flask.

6.5.2 Preparation of standard matching solutions. Into a series of six 250 ml beakers, each containing 10.0 ml of the potassium hydrogen carbonate solution (6.3.3), add to each 18.9 ml of the hydrochloric acid solution (6.3.1) and then measure accurately, from a 10 ml burette, the volumes of the standard sodium chloride solution (6.3.4) shown in the following table:

Standard sodium chloride solution (6.3.4)	Equivalent sodium hydroxide (NaOH) content
ml	mg
0 ^a	0
2.0	4.0
4.0	8.0
6.0	12.0
8.0	16.0
10.0	20.0

^a Blank standard matching solution.

Treat the contents of each beaker as follows.

Heat to boiling and cool. Transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

6.5.3 Adjustment of the apparatus. Switch on the current a sufficient time in advance to ensure stabilization. Turn on the gas supplies and ignite the burner. If the flame photometer (6.4.1) is used, insert the sodium filter. If the flame spectrophotometer (6.4.2) is used, set the monochromator to a wavelength of about 589 nm. Aspirate water into the flame and set the instrument to zero reading. Aspirate the most concentrated standard matching solution (6.5.2) into the flame and adjust the instrument sensitivity to give a suitable response. In the case of the flame spectrophotometer it may be necessary to offset the burner to reduce the sensitivity.

6.5.4 Photometric measurements. Aspirate the series of standard matching solutions (6.5.2) into the flame and measure the response for each. Spray water through the burner after each measurement. Take care to keep the aspiration rate constant throughout this series of measurements.

6.5.5 Preparation of the calibration graph. Plot a graph having, for example, the number of equivalent milligrams of sodium hydroxide contained in 1 000 ml of the standard matching solutions as abscissae and the corresponding values of the measured response, less the measured value for the blank standard matching solution, as ordinates.

NOTE It is essential that the calibration graph obtained is rectilinear.

6.5.6 Determination

6.5.6.1 Preparation of the test solution. Dilute the test portion in the 100 ml one-mark volumetric flask (6.5.1) to the mark with water and mix.

Using a pipette, transfer 25.0 ml of this solution into a 150 ml conical flask and titrate with the hydrochloric acid solution (6.3.1) using the methyl orange solution (6.3.2) as indicator. Note the volume of the hydrochloric acid solution used in the titration, X ml, and discard the titrated solution.

Transfer a further 25.0 ml of the solution from the 100 ml one-mark volumetric flask into a 1 000 ml one-mark volumetric flask, add $(10.0 + X)$ ml of the hydrochloric acid solution (6.3.1), dilute to the mark with water and mix.

6.5.6.2 Photometric measurements. Immediately after making the photometric measurements on the standard matching solutions (6.5.4), determine in a similar manner the response from the test solution (6.5.6.1). Subtract from it the value for the blank standard matching solution (6.5.2) and, using this corrected value, read from the calibration graph the sodium content of the test solution (6.5.6.1) expressed as milligrams of sodium hydroxide.

6.6 Expression of results. The sodium content, expressed as a percentage by mass of sodium hydroxide (NaOH), is given by the following formula:

$$\frac{m_1}{1000} \times \frac{500}{2.5 \times m_0} \times 100 = \frac{20 m_1}{m_0}$$

where

m_1 is the mass of sodium, expressed as sodium hydroxide, in the test solution (6.5.6.1) (in mg)

m_0 is the mass of sample in 500 ml of the solution A (3.4.2) (in g)

7 Determination of chloride content

7.1 Field of application. The method is applicable to products having chloride contents, expressed as potassium chloride (KCl), in the range 4 mg/kg to 100 mg/kg.

7.2 Principle. Thiocyanate (SCN) ions, derived from a solution of mercury (II) thiocyanate, are displaced by the chloride (Cl) ions contained in the test solution when the two solutions are mixed. The displaced (SCN) ions are reacted with a solution of iron (III) nitrate to form red coloured iron (III) thiocyanate.

The intensity of the developed colour is measured photometrically at a wavelength of about 450 nm.

7.3 Reagents. The reagents used shall be of recognized analytical quality. Only double-distilled water, or water of equivalent purity, shall be used throughout. The preparation and storage of the reagents, as well as the sampling and determination, shall take place in an atmosphere free from chlorine and hydrochloric acid.

7.3.1 Nitric acid, ρ approximately 1.42 g/ml, about 70 % m/m solution or approximately 16N solution, having a chloride (Cl) content not exceeding 0.5 mg/kg.

7.3.2 Iron (III) nitrate, solution corresponding to 8 g of iron per litre. Pour 80 ml of water into a 500 ml conical flask and add 4.0 g of pure (not less than 99.5 %) iron wire. Cautiously add 80 ml of the nitric acid solution (7.3.1). Heat and then boil in a ventilated fume cupboard until the reaction is complete and nitrous fumes have been completely eliminated. Decolorize the solution by adding a few drops of 30 % m/m hydrogen peroxide solution and boil again for a few minutes. Cool, transfer quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution immediately before use.

7.3.3 Mercury (II) thiocyanate, 0.5 g/l solution. Weigh, to the nearest 0.001 g, 0.100 g of mercury (II) thiocyanate $[\text{Hg}(\text{SCN})_2]$ and dissolve in 180 ml of water at a temperature of 50 °C, while stirring. Cool, filter, collecting the filtrate in a 200 ml one-mark volumetric flask, dilute to the mark and mix. Prepare this solution immediately before use.

7.3.4 Sodium chloride, standard solution corresponding to 0.100 g of chloride per litre. Weigh, to the nearest 0.001 g, 0.165 g of sodium chloride, previously dried at a temperature of 500 °C for 1 h and then cooled, dissolve in water, dilute to the mark in a 1 000 ml one-mark volumetric flask and mix.

1 ml of this standard solution contains 0.1 mg of Cl.

7.3.5 Sodium chloride, standard solution corresponding to 10 mg of chloride per litre. Pipette 20.0 ml of the standard sodium chloride solution (7.3.4) into a 200 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.