# INTERNATIONAL STANDARD 3194

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# Potassium hydroxide for industrial use — Determination of sulphur compounds — Method by reduction and titrimetry

*Hydroxyde de potassium à usage industriel — Dosage des composés soufrés — Méthode par réduction et titrimétrie*



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## FOREWORD

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International Standard ISO 3194 was drawn up by Technical Committee ISO/TC 47, *Chemistry*, and circulated to the Member Bodies in November 1973.



It has been approved by the Member Bodies of the following countries :



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No Member Body expressed disapproval of the document.



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# Potassium hydroxide for industrial use — Determination of sulphur compounds — Method by reduction and titrimetry

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a reduction and titrimetric method for the determination of sulphur compounds in potassium hydroxide for industrial use.

The method is applicable to products of which the content of sulphur compounds, expressed as sulphate ($SO_4$), is equal to or greater than 5 mg/kg.

## 2 REFERENCE

ISO 2466, *Potassium hydroxide for industrial use — Sampling — Test sample — Preparation of the main solution for carrying out certain determinations.*



## 3 PRINCIPLE

Reduction of the sulphur compounds to hydrogen sulphide by heating with a mixture of hydriodic acid and hypophosphorous acid.

Absorption of the hydrogen sulphide, entrained in a current of oxygen-free nitrogen, in a mixture of sodium hydroxide and acetone.

Titration of the sulphide with standard volumetric mercury(II) nitrate solution in the presence of dithizone as indicator.

## 4 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

**4.1 Acetone.**

**4.2 Nitrogen,** oxygen-free.

**4.3 Sodium hydroxide,** approximately 1 N solution.

**4.4 Potassium permanganate and mercury(II) chloride** solution, to purify the nitrogen (4.2).

Dissolve first 2 g of potassium permanganate ($KMnO_4$) and then 7 g of mercury(II) chloride ($HgCl_2$), in 100 ml of water and filter the solution.

**4.5 Pyrogallol** solution, to purify the nitrogen (4.2).

Dissolve 15 g of pyrogallol in 25 ml of water and add, while cooling, 150 ml of a 30 % (*m/m*) potassium hydroxide solution.

**4.6 Reduction solution**

Place in the flask (J) of the apparatus (5.3), shaking after each addition :

— 50 ml of hypophosphorous acid ($H_3PO_2$), $\rho$ approximately 1,21 g/ml, about 50 % (*m/m*) solution;

— 100 ml of hydrochloric acid, $\rho$ approximately 1,19 g/ml, about 38 % (*m/m*) solution;

— 120 ml of hydriodic acid, $\rho$ approximately 1,97 g/ml, about 67 % (*m/m*) solution.

Assemble the flask and the reflux condenser (K) then, while passing a slow flow of the nitrogen (4.2), boil for 4 h.

Cool to room temperature under a flow of the nitrogen (4.2) and store the reagent away from direct sunlight in an amber glass bottle previously flushed with the nitrogen (4.2) and fitted with a ground glass stopper.

**4.7 Sodium sulphate,** 0,001 M standard reference solution.

Weigh, to the nearest 0,000 1 g, 0,142 0 g of anhydrous sodium sulphate, previously dried at 110 °C and cooled in a desiccator. Introduce into a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark and mix.

1 ml of this solution corresponds to 96 $\mu$g of $SO_4$.

**4.8 Mercury(II) nitrate,** 0,05 M standard volumetric solution (= 0,1 N)

Dissolve 10,85 ± 0,01 g of mercury(II) oxide (HgO) in 10 ml of nitric acid solution, $\rho$ approximately 1,40 g/ml, about 68 % (*m/m*) solution, dilute to 1 000 ml with water and mix.

NOTE — The strength of the solution thus prepared is sufficiently exact for the small quantities of sulphur compounds to be determined and standardization is therefore unnecessary.

In most laboratories, however, a precisely 0,1 N standard volumetric solution, commonly used for the mercurimetric determination of chlorides, will be available.

**4.9 Mercury(II) nitrate,** 0,001 M standard volumetric solution (= 0,002 N).

Dilute 20,00 ml of the standard volumetric mercury(II) nitrate solution (4.8) to the mark in a 1 000 ml one-mark volumetric flask.

Prepare this solution at the time of use.

**4.10 Dithizone,** 0,5 g/l solution in the acetone (4.1).

## 5 APPARATUS

Ordinary laboratory apparatus and

**5.1 Microburette,** capacity 5 ml, graduated in 0,01 ml (G).

**5.2 Apparatus for reduction and distillation** of which all the components are fitted together with ground glass joints. A typical apparatus is shown in figure 1 and comprises :

**5.2.1** *Wash bottles* (A and B), Drechsel type, capacity 50 ml.

**5.2.2** *Conical flasks* (C), capacity 100 ml.

**5.2.3** *Reflux condenser* (D).

**5.2.4** *Absorption vessel* (E), internal diameter 25 mm and height 100 mm.

**5.2.5** *Dropping funnel* (F), capacity 50 ml.

**5.2.6** *Stopcocks* (1, 2, 3 and 4).

**5.3 Apparatus for preparation of the reduction solution** (4.6).

A typical apparatus is shown in figure 2, and comprises :

**5.3.1** *Flask, three-necked* (J), capacity 500 ml.

**5.3.2** *Reflux condenser* (K).

**5.3.3** *Nitrogen supply tube* (L).

## 6 PROCEDURE

### 6.1 Test portion

Weigh, to the nearest 0,01 g, a mass of the test sample (see ISO 2466), solid or liquid, not exceeding 5 or 10 g respectively, into a dried conical flask (C). Fit with a stopper.

### 6.2 Check test

The purpose of this test is to check the gas-tightness and functioning of the apparatus (reduction of sulphur compounds and quantitative recovery of the hydrogen sulphide liberated).

Transfer in turn :

— to the wash bottle (A), 25 ml of the potassium permanganate and mercury(II) chloride solution (4.4);

— to the wash bottle (B), 25 ml of the pyrogallol solution (4.5);

— to the absorption vessel (E), 5 ml of the sodium hydroxide solution (4.3), 5 ml of the acetone (4.1) and 0,1 ml of the dithizone solution (4.10);

— to a dried conical flask (C), 2,00 ml of the standard reference sodium sulphate solution (4.7) and a few glass beads;

— to the dropping funnel (F), 50 ml of the reducing solution (4.6);

— to the microburette (G), the standard volumetric mercury(II) nitrate solution (4.9).

Assemble the apparatus taking care to smear the ground joints with a silicone grease and to tighten them with suitable spring-clips in order to ensure perfect gas-tightness. Pass the nitrogen (4.2) through stopcocks (2) and (4), at a speed of about 2 bubbles per second. After 5 min, run the mercury(II) nitrate solution (4.9), drop by drop, into the absorption vessel (E) until the indicator changes from yellow to red.



Open stopcocks (1) and (3) to allow the reducing solution (4.6) to run into the conical flask (C), leaving a few millimetres of liquid in the dropping funnel (F), then close the two stopcocks.

Start the condenser (D) and, while continuing the flow of nitrogen, boil the solution gently in the conical flask (C) for at least 30 min. The presence of hydrogen sulphide is shown by a colour change of the indicator from red to yellow.

Stop the boiling and, while maintaining the flow of nitrogen, titrate the sulphide in the absorption vessel (E) with the standard volumetric mercury(II) nitrate solution (4.9) contained in the microburette (G) until the indicator changes from yellow to red.

The result of the check test is considered satisfactory if the volume of the standard volumetric mercury(II) nitrate solution (4.9) used for the titration is between 1,90 and 2,10 ml, after subtraction of the blank test result (6.3). Otherwise check the apparatus for leaks.

### 6.3 Blank test

Carry out a blank test under the same conditions as the check test (6.2), but using 2,00 ml of water instead of 2,00 ml of the standard reference sodium sulphate solution (4.7).

### 6.4 Determination

Carry out the determination under the same conditions as the check test (6.2), using the test portion (6.1) instead of the 2,00 ml of the standard reference sodium sulphate solution (4.7).

## 7 EXPRESSION OF RESULTS

The content of sulphur compounds, expressed as milligrams of sulphate ($SO_4$) per kilogram, is given by the formula

$$(V_1 - V_0) \times \frac{1}{1\,000} \times \frac{1\,000}{m} \times 96 = \frac{(V_1 - V_0) \times 96}{m}$$

where

$V_0$ is the volume, in millilitres, of the standard volumetric mercury(II) nitrate solution (4.9) used for the blank test;

$V_1$ is the volume, in millilitres, of the standard volumetric mercury(II) nitrate solution (4.9) used for the determination;

$m$ is the mass, in grams, of the test portion (6.1);

96 is the mass, in micrograms, of $SO_4$ corresponding to 1 ml of the standard volumetric mercury(II) nitrate solution (4.9).

## 8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or in the International Standard to which reference is made, or regarded as optional.

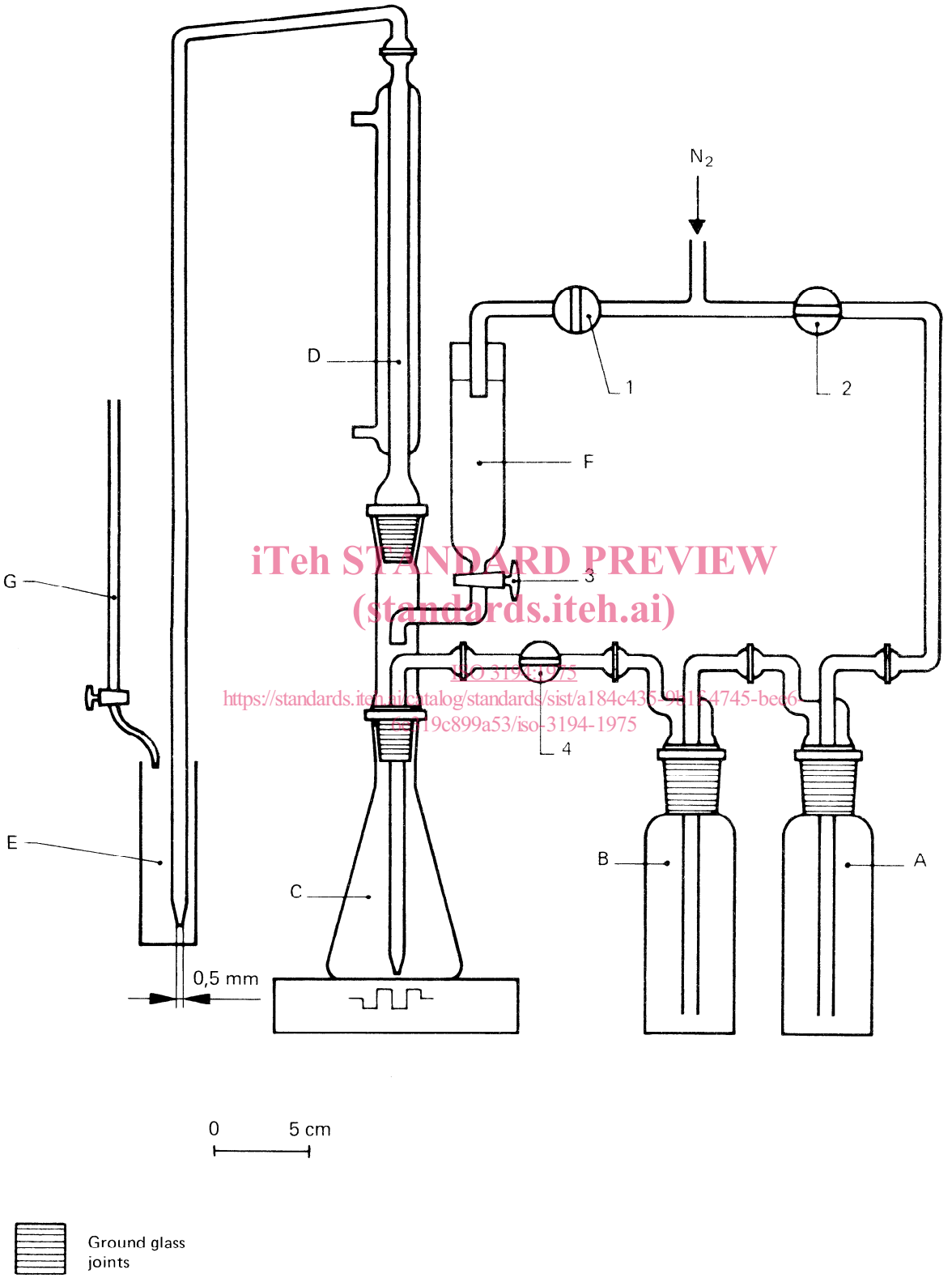




FIGURE 1 – **Typical apparatus for the determination of sulphur compounds**

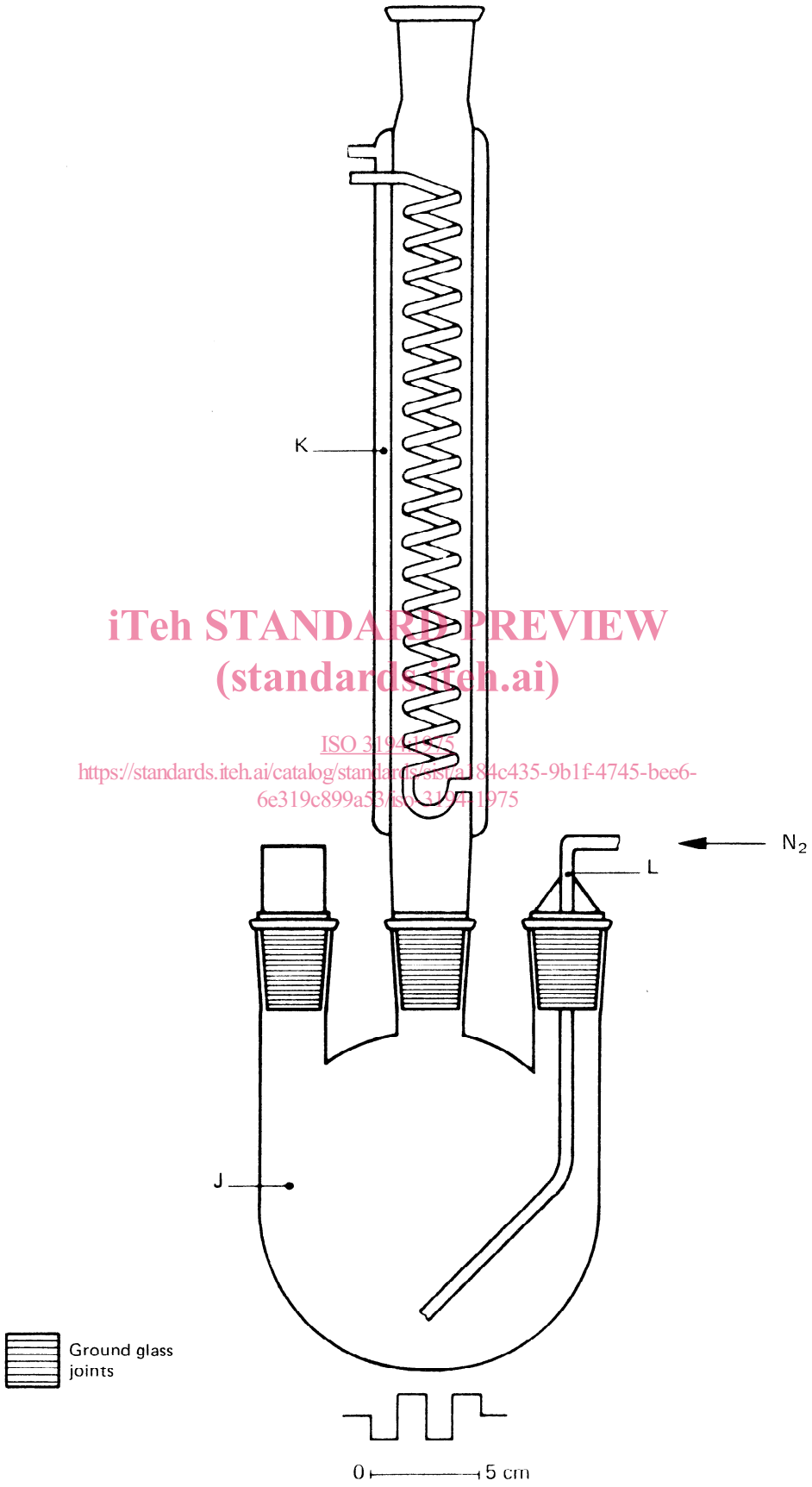




FIGURE 2 – **Typical apparatus for the preparation of the reducing solution**

ANNEX

## ISO PUBLICATIONS RELATING TO POTASSIUM HYDROXIDE FOR INDUSTRIAL USE

ISO 990 – Method of assay.

ISO/R 991 – Determination of the carbon dioxide content, expressed as potassium carbonate – Gas-volumetric method.

ISO 992 – Determination of chloride content – Mercurimetric method.

ISO/R 993 – Determination of sulphate content – Barium sulphate gravimetric method.

ISO 994 – Determination of iron content – 1,10-Phenanthroline photometric method.

ISO 995 – Determination of silica content – Reduced silicomolybdic complex photometric method.

ISO/R 996 – Determination of silica content – Gravimetric method by precipitation of the quinoline-silicomolybdic complex.

ISO/R 997 – Determination of calcium – EDTA complexometric method.

ISO/R 998 – Determination of water-insoluble matter.

ISO 1550 – Determination of sodium content – Flame emission spectrophotometric method.

ISO/R 1551 – Determination of sodium – Gravimetric method using uranyl acetate and magnesium acetate.

ISO 2466 – Sampling – Test sample – Preparation of the main solution for carrying out certain determinations.



ISO 2900 – Determination of carbon dioxide content – Titrimetric method.

ISO 3177 – Determination of chloride content – Photometric method.



ISO 3194 – Determination of sulphur compounds – Method by reduction and titrimetry.

ISO 3698 – Determination of calcium and magnesium contents – Flame atomic absorption spectrophotometric method.