INTERNATIONAL STANDARD 5143

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Sodium carbonate for industrial use — Determination of sulphur compounds content — Method by reduction and titrimetry

Carbonate de sodium à usage industriel — Dosage des composés soufrés — Méthode par réduction et titrimétrie

First edition — 1977-11-01

UDC 661.833.622 : 546.22 : 543.24

Ref. No. ISO 5143-1977 (E)

Descriptors : chemical compounds, sodium carbonate, chemical anslysis, determination of content, sulphates, volumetric analysis, reduction analysis.

Price based on 6 pages

FOREWORD

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5143 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in July 1976.

It has been approved by the member bodies of the following countries:

Austria	India	Spain
Belgium	Israel	Switzerland
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Chile	Mexico	Turkey
Czechoslovakia	Netherlands	United Kingdom
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Hungary	South Africa, Rep. of	

The member bodies of the following countries expressed disapproval of the document on technical grounds:

Italy
U.S.S.R.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

Printed in Switzerland

Sodium carbonate for industrial use — Determination of sulphur compounds content — Method by reduction and titrimetry

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method, by reduction and titrimetry, for the determination of sulphur compounds content of sodium carbonate for industrial use.

The method is applicable to products having a sulphur compounds content, expressed as sulphate (SO_4^{2-}), equal to or greater than 5 mg/kg.

2 REFERENCE

ISO 739, *Sodium carbonate for industrial use — Preparation and storage of test samples.*

3 PRINCIPLE

Progressive neutralization, with evolution of carbon dioxide, by adding slowly a mixture of hydriodic acid and hypophosphorous acid. Reduction of sulphur compounds to hydrogen sulphide by heating with this reducing solution.

Distillation of hydrogen sulphide, entrainment in a current of oxygen-free nitrogen and absorption in a mixture of acetone and sodium hydroxide solution.

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

4 REAGENTS

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

4.1 Acetone.

4.2 Nitrogen, free from oxygen.

4.4 Sodium hydroxide, approximately 10 N solution.

4.4 Sodium hydroxide, approximately 1 N solution.

4.5 Reducing solution.

Place the flask (F) of the apparatus (5.3), swirling after each addition :

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

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

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

Assemble the reflux condenser (G), flask (F) and inlet tube (H). Then, while passing a slow stream of the nitrogen (4.2), boil under reflux for 4 h.

Cool to ambient temperature, under a flow of the nitrogen, and store the reagent away from direct sunlight in an amber glass bottle, previously purged with the nitrogen, fitted with a ground glass stopper.

4.6 Sodium sulphate, 0,001 M (= 0,002 N) standard reference solution.

Weigh, to the nearest 0,001 g, 0,142 0 g of anhydrous sodium sulphate, previously dried at 110 °C and cooled in a desiccator. Transfer quantitatively to 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 μg of SO_4.

4.7 Mercury(II) nitrate, 0,05 M (= 0,1 N) standard volumetric solution.

Weigh 10,85 ± 0,01 g of mercury(II) oxide (HgO), place in a beaker of suitable capacity (100 ml for example) and dissolve in 10 ml of nitric acid solution, ρ approximately 1,40 g/ml, about 68 % (*m/m*) solution. Dilute the solution, transfer it quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

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

Place 20,00 ml of the standard volumetric mercury(II) nitrate solution (4.7) in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution just before use.

NOTE — The concentration of the solutions (4.7 and 4.8) prepared as described above are sufficiently exact, taking into consideration the small amounts of sulphur compounds to be determined. Standardization is therefore unnecessary.

In most laboratories, an exactly 0,05 M (= 0,1 N) standard volumetric mercury(II) nitrate solution will be available, this solution being commonly used for the mercurimetric determination of chlorides.

4.9 (Phenylazo)thioformic acid, 2-phenylhydrazide (dithizone), 0,5 g/l solution in the acetone (4.1).

Renew this solution after 2 weeks.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Burette (E), of capacity 5 ml, graduated in 0,01 ml.

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

5.2.1 *Conical flask* (A) of capacity 100 ml.

5.2.2 *Reflux condenser* (B).

5.2.3 *Absorption vessel* (C), of height 100 mm and internal diameter 25 mm.

5.2.4 *Dropping funnel* (D), of capacity 50 ml.

5.2.5 *Stopcocks* (1), (2) and (3).

5.3 Apparatus for the preparation of the reducing solution (4.5).

A typical apparatus is shown in figure 2 and comprises

5.3.1 *Three-necked flask* (F), of capacity 500 ml.

5.3.2 *Reflux condenser* (G), spiral type.

5.3.3 *Inlet tube* (H), for nitrogen.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,01 g, a mass of the test sample (see ISO 739) containing not more than 5 g of Na_2CO_3 into the dried conical flask (A).

6.2 Check test

The purpose of this test is to check the gas tightness and functioning of the apparatus (5.2) (reduction of sulphur compounds and quantitative recovery of the hydrogen sulphide liberated).

Place respectively

— into the absorption vessel (C) : 5 ml of the sodium hydroxide solution (4.4), 5 ml of the acetone (4.1) and 0,1 ml of the dithizone solution (4.9);

— into the dried conical flask (A) : 2,00 ml of the standard reference sodium sulphate solution (4.6) and a few glass beads;

— into the dropping funnel (D) : 50 ml of the reducing solution (4.5);

— into the burette (E) : the standard volumetric mercury(II) nitrate solution (4.8).

Assemble the apparatus (5.2), taking care to smear the ground glass joints lightly with a silicone grease and to tighten them with suitable clips to ensure perfect gas tightness. Pass the nitrogen (4.2) through stopcock (3) at a rate of about 2 bubbles per second. After 5 min, run the mercury(II) nitrate solution (4.8), drop by drop, into the absorption vessel (C) until the colour of the indicator changes from yellow to red.

Open stopcocks (1) and (2) in order to allow the reducing solution (4.5) to flow into the conical flask (A), leaving a few millimetres of liquid in the dropping funnel (D), and then close both stopcocks.

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

NOTE — Development of a blue-green coloration indicates that a large quantity of hydrochloric acid has been entrained and the check test should be repeated. This will only occur exceptionally and will probably result from an accident. If it were, however, to occur on repetition of this test, it would, *in that case,* be advisable to place one or two wash-bottles containing a 100 g/l solution of sodium dihydrogenphosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) between the condenser (B) and the absorption vessel (C) in order to absorb the acid vapours without retaining the hydrogen sulphide.

Stop the boiling and, while continuing the flow of nitrogen, titrate the sulphide in the absorption vessel (C) with the standard volumetric mercury(II) nitrate solution (4.8) contained in the burette (E), until the colour of 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 used for the titration is between 1,90 and 2,10 ml after subtraction of the blank test result (6.3). If low results are obtained, this may be due to the presence of leaks in the apparatus, oxygen in the nitrogen, or exhaustion of the reducing solution. Check these sources of error and repeat the check test until satisfactory results are obtained.

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 (4.6).

6.4 Determination

Carry out the determination under the same conditions as the check test (6.2), subject, however, to the following amendments :

— substitute the test portion (6.1) for the 2,00 ml of the standard reference sodium sulphate solution (4.6);

– run the reducing solution (4.5) very slowly, drop by drop, into the conical flask (A) in order to avoid sudden evolution of carbon dioxide;

– place 1 ml of the sodium hydroxide solution (4.3) in the absorption vessel (C) to render the absorbing solution alkaline before boiling the solution in the conical flask (A).

7 EXPRESSION OF RESULTS

The sulphur compounds content, expressed as milligrams of sulphate (SO_4^{2-}) 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 (4.8) used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric mercury(II) nitrate solution (4.8) 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 (4.8).

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.

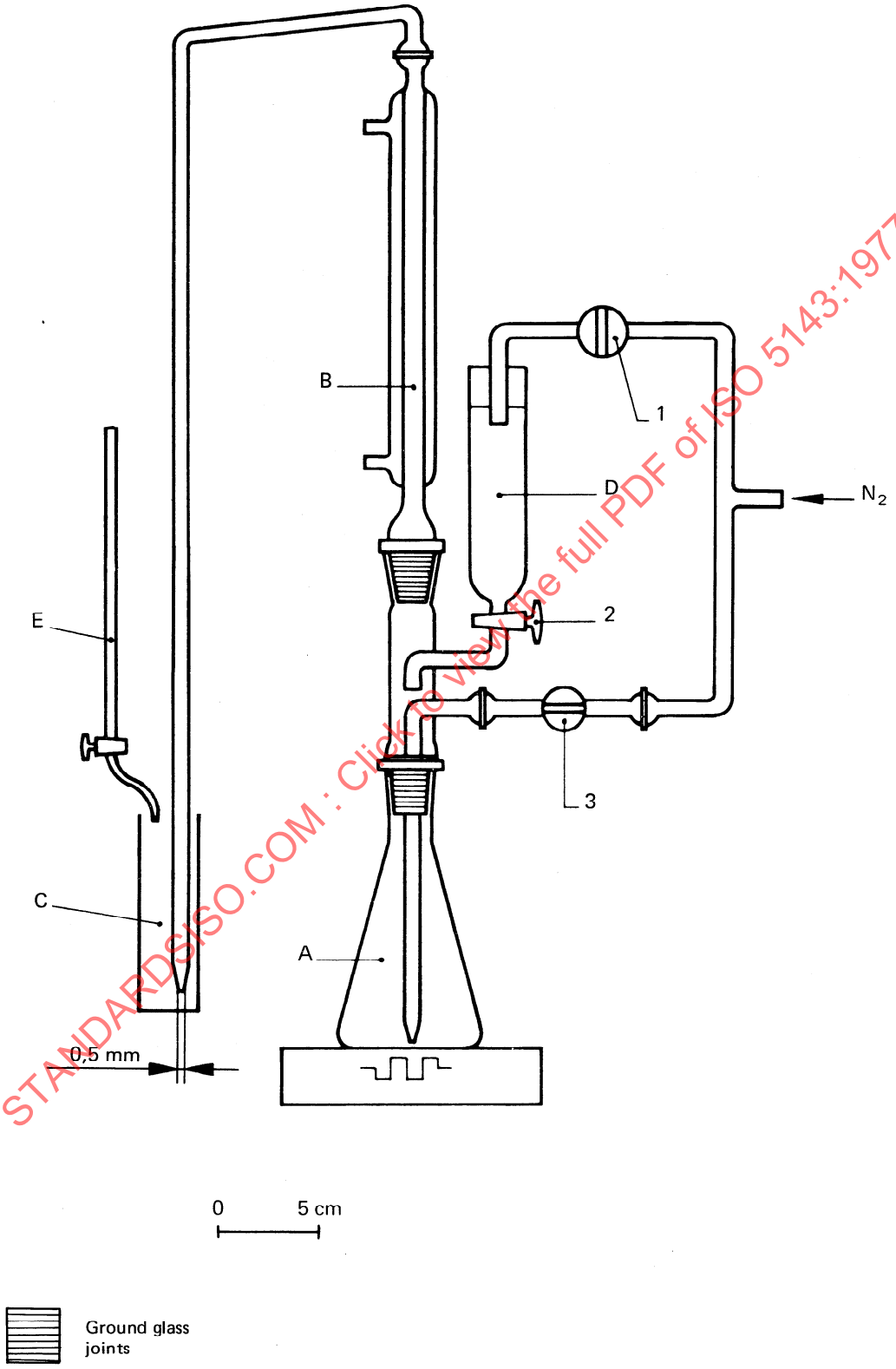

FIGURE 1 — **Typical apparatus for the determination of sulphur compounds**