

# International Standard



# 4493

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

## **Metallic powders — Determination of hydrogen reducible oxygen content**

*Poudres métalliques — Détermination de la teneur en oxygène réductible par l'hydrogène*

**First edition — 1981-08-15**

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**UDC 621.762 : 669-492.2 : 543**

**Ref. No. ISO 4493-1981 (E)**

**Descriptors :** pulverulent products, metallic powder, tests, determination of content, hydrogen, oxygen, Karl Fischer reagent.

## 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 4493 was developed by Technical Committee ISO/TC 119, *Powder metallurgy*, and was circulated to the member bodies in November 1979.

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

Austria	Italy	Spain
Bulgaria	Japan	Sweden
Canada	Korea, Rep. of	United Kingdom
Czechoslovakia	Poland	USA
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Germany, F. R.	Romania	
India	South Africa, Rep. of	

The member body of the following country expressed disapproval of the document on technical grounds :

China

# Metallic powders — Determination of hydrogen reducible oxygen content

## 1 Scope and field of application

This International Standard specifies a method for the determination of the hydrogen reducible oxygen content of metallic powders free of admixed pressing lubricant.

The method is applicable to the metal powders listed in table 2 and for the determination of oxygen contents between 0,05 and 3 % (*m/m*). It is not applicable to the metal powders in the upper part of table 2 when they contain carbon.<sup>1)</sup>

## 2 Reference

ISO 760, *Determination of water — Karl Fischer method (General method)*.

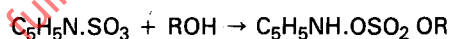
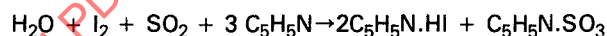
## 3 Principle

**3.1** Heating a test portion in a stream of pure and dry hydrogen. Absorption of the water, formed by reaction of the metal oxide with the hydrogen, in methanol, and titration with Karl Fischer reagent. Determination of the end-point electrometrically, using the dead-stop technique.

**3.2** If the powder contains moisture, the test portion is heated to 150 °C in dry nitrogen before the reduction in hydrogen is carried out; otherwise, the moisture would react with the Karl Fischer reagent.

**3.3** As the apparatus may not be perfectly gas tight, and as the dried hydrogen and nitrogen may still contain very small amounts of water and oxygen, a blank test is carried out.

**3.4** The determination of water by the Karl Fischer method is based on the fact that iodine and sulphur dioxide, in a pyridine/methanol or pyridine/2-methoxyethanol mixture, react with water according to the equations



The Karl Fischer reagent consists of iodine, sulphur dioxide and pyridine dissolved in methanol or 2-methoxyethanol (ethylene glycol monomethyl ether). The end-point is reached when all the water has reacted and free iodine appears in the solution, i.e. when the pale yellow solution turns to orange red (visual end-point).

ISO 760 describes in detail the preparation and standardization of the Karl Fischer reagent and the different types of equipment. The procedure given in this International Standard is only sufficient to ensure that the method can be understood.

## 4 Reagents

**4.1** Methanol, water free.

**4.2** Karl Fischer reagent, equivalent to 3 to 5 mg of oxygen per millilitre.

**WARNING —** Karl Fischer reagent contains four toxic compounds: iodine, sulphur dioxide, pyridine and methanol. It is important to avoid direct contact and especially inhalation. Following accidental spillage, rinse with plenty of water.

1) If carbon is present, some metal oxides may be reduced by the carbon, producing carbon monoxide or carbon dioxide. These oxides may otherwise have been reduced by the hydrogen. If this carbon reduction occurs, a lower result will be obtained for the hydrogen reducible oxygen content. In such cases the method may be used possibly with some modifications by agreement between the parties concerned. One solution is to convert the carbon monoxide or dioxide to methane and water by passing the gases over activated nickel at a temperature of 380 °C.

The titre of the Karl Fischer reagent may be determined by either of the following methods :

- a) addition of 20 to 30 mg of water, weighed to the nearest 0,1 mg;
- b) addition of 100 to 300 mg, weighed to the nearest 0,1 mg, of sodium tartrate dihydrate [certified material containing theoretically 15,66 % (m/m) of water, corresponding to 13,92 % (m/m) of oxygen], ground to fine powder and dried at  $155 \pm 5$  °C to constant mass.

The titre shall be calculated to the nearest 0,01 mg of oxygen per millilitre.

NOTE — See ISO 760 for methods of standardization.

**4.3 Hydrogen**, having a maximum oxygen content of 0,005 % and a dew point not exceeding - 45 °C.

**4.4 Nitrogen**, having a maximum oxygen content of 0,005 % and a dew point not exceeding - 45 °C. Argon may be substituted for nitrogen.

**4.5 Desiccant** : granular anhydrous aluminium sodium silicate, activated silica gel, or magnesium perchlorate.

## 5 Apparatus

NOTE — The arrangement of the apparatus is shown schematically in figure 1.

Ordinary laboratory apparatus and

**5.1 Source of hydrogen (A)**, fitted with a pressure regulating valve, a flow control valve, and a flow meter.

**5.2 Catalytic purifier (B)**, for the hydrogen.

**5.3 Source of nitrogen (C)** fitted with a pressure regulating valve, a flow control valve, and a flow meter.

**5.4 Gas selecting valve (D)**.

**5.5 Gas drying unit (E)**, containing one of the desiccants specified in 4.5.

**5.6 Reduction tube (F)**, gas tight, made of quartz, closed at one end, having a diameter of 27 to 30 mm and a length of about 400 mm; it also comprises two quartz tubes of diameter 5 to 6 mm and lengths 60 to 80 mm and 200 to 240 mm, respectively, arranged as shown in figure 2.

**5.7 Two furnaces (G)**, one for drying the test portion and one for reduction, with temperature control systems capable of maintaining the temperature in the part of the tube containing the boat within the specified temperature tolerances.

If available, one furnace combining both these functions may be used.

**5.8 Boats (H)**, preferably high alumina ceramic, with a polished surface and of a suitable size such that no more than half is filled by the test portion. These boats shall be conditioned in hydrogen at 900 to 1 100 °C for at least 1 h and stored in a desiccator before use.

**5.9 Automatic burette (J)**, of capacity 25 ml and with a fine point, graduated in 0,05 ml divisions, and protected from atmospheric moisture by a guard tube filled with one of the desiccants specified in 4.5.

**5.10 Titration flask (K)**, comprising a 300 ml conical flask containing platinum electrodes and a magnetic stirrer.

**5.11 End-point detector (L)**.

A circuit diagram of an electrometric end-point detector, utilizing the dead-stop technique, is shown in figure 3.

NOTE — Items (J), (K) and (L) are given as examples with which satisfactory results have been obtained. Modifications to these or to any commercially available Karl Fischer titration equipment may be made, provided that the operating requirements are fulfilled (see ISO 760).

**5.12 Stop-watch**, for determination of the titration end-point.

**5.13 Timer**.

**5.14 Blower** (for example a hair-dryer), for cooling the tube.

## 6 Sampling

**6.1** The powder shall be tested in the as-received condition.

**6.2** The analysis shall be carried out on two test portions.

## 7 Procedure

### 7.1 Test portion

Weigh, to the nearest 0,000 1 g, a mass of test portion, according to the expected hydrogen reducible oxygen content, as indicated in table 1.

Table 1

Expected hydrogen reducible oxygen content % (m/m)	Mass of test portion g
from 0,05 to 0,5	5
from 0,5 to 2,0	2
from 2,0 to 3,0	1

## 7.2 Test conditions

For each apparatus and for each type of powder, determine experimentally the best reduction temperature and time so that the reduction is complete and the procedure is not unnecessarily prolonged. (The values in table 2 are given for guidance only.)

Also determine the best drying time at 150 °C in dry nitrogen.

Table 2

Metal powder	Reduction temperature °C	Reduction time min
Iron and steel	1 100 ± 50	20
Cobalt	900 ± 50	20
Nickel	900 ± 50	20
Copper	900 ± 50	20
Molybdenum	1 100 ± 50	20
Tungsten	1 100 ± 50	20
Powders for hardmetals	900 ± 50	20

## 7.3 Preparation of the apparatus

Condition and check the reduction tube and apparatus as follows:

**7.3.1** Set the temperature of the heating zone to the reduction temperature, leaving the reduction tube outside the furnace.

**7.3.2** Rinse the burette (5.9) with the Karl Fischer reagent (4.2) to make sure that no moisture, which could change the titre of the reagent, is present, discard the rinsings and charge the burette with the Karl Fischer reagent (4.2).

**7.3.3** Add the methanol (4.1) to the titration flask taking care to adjust the liquid level so that the inlet tube and the electrodes are below the surface of the liquid. Approximately 70 ml are required. Start the magnetic stirrer and titrate with the Karl Fischer reagent to the visual end-point to neutralize any traces of water in the methanol.

**7.3.4** Short-circuit the electrodes by switch S of the electrometric end-point detector (5.11) (see figure 3) and adjust the variable resistor R to give a current of 120 µA on the microammeter M. Reopen switch S.

**7.3.5** Adjust the nitrogen flow to at least 30 l/h and allow it to flow for 10 min. Change the gas flow from nitrogen to hydrogen by valve D and adjust the flow to at least 30 l/h.

NOTE — Once the gas flow has commenced, it shall not be interrupted until the whole series of determinations is complete.

**7.3.6** Insert the reduction tube (5.6) into the furnace and leave for 10 min. Change the gas flow from hydrogen to nitrogen.

**7.3.7** Withdraw the tube and cool it with the blower (5.14) to room temperature. Again titrate the methanol to the visual end-point to neutralize any traces of water released during conditioning.

**CAUTION — Do not open the reduction tube or stop the hydrogen flow while the tube is still hot.**

**7.3.8** Check the condition and gas tightness of the apparatus by the blank test specified in 7.4.

## 7.4 Blank test

Blank tests, using an empty boat, shall be performed with every series of determinations by following the procedures specified in 7.5.1 to 7.5.6.

An apparatus in good condition shall yield a result for the blank test of approximately 1 mg of oxygen for a heating period of 20 min. If the result is much higher, or if variable results are obtained, the apparatus shall be checked for leaks.

## 7.5 Determination

**7.5.1** Open the reduction tube (5.6) and insert the boat containing the weighed test portion (or empty boat for the blank test). Close the tube and purge with dry nitrogen at a flow rate of at least 30 l/h to expel the air introduced with the test portion. If the purge time has not been previously established, allow 10 min. Titrate the methanol to the visual end-point.

**7.5.2** Adjust the nitrogen flow to 15 l/h and insert the tube into the furnace at a temperature of 150 ± 10 °C and start the timer (5.13).

**7.5.3** At the end of the drying period, titrate the methanol to the end-point using the electrometric end-point detector (5.11) after having previously adjusted the detector as described in 7.3.4. Record the volume of Karl Fischer reagent in the burette and the drying time.

**7.5.4** Using valve D, change the gas flow from nitrogen to hydrogen, adjust the flow to 15 l/h, and insert the tube into the furnace maintained at the reduction temperature. Start the timer.

**7.5.5** At the end of the reduction period, titrate the methanol to the end-point using the electrometric end-point detector (5.11). Read the burette and record the titration volume,  $V_1$ , in millilitres. Record the reduction time.

**7.5.6** Using valve D, change the gas flow from hydrogen to nitrogen and withdraw the tube from the furnace. Cool the tube to room temperature, using a blower if required, open the tube and extract the boat.

## 8 Expression of results

8.1 The hydrogen reducible oxygen content, expressed as a percentage by mass, is given by the formula

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

where

$V_1$  is the volume, in millilitres, of Karl Fischer reagent used for titration of the test portion;

$V_2$  is the volume, in millilitres, of Karl Fischer reagent used for titration in the blank test;

$m$  is the mass, in milligrams, of the test portion;

$n$  is the titre, in milligrams of oxygen per millilitre, of the Karl Fischer reagent.

8.2 Calculate the mean of the two determinations and report the result to the nearest 0,02 % (m/m) for hydrogen reducible oxygen contents up to and including 0,8 % (m/m) and to the nearest 0,05 % (m/m) for contents greater than 0,8 % (m/m), provided that the requirements of 8.3 are satisfied.

8.3 The difference between the results of the two determinations shall not exceed 0,04 % (absolute value) when the hydrogen reducible oxygen content is less than 0,8 % (m/m), or 5 %

of the mean value when the hydrogen reducible oxygen content is equal to or greater than 0,8 % (m/m).

If the difference exceeds these values, the test shall be repeated, attention being given to the reproducibility of the blank test, the reduction time and all the other precautions stated.

## 9 Test report

The test report shall include the following information :

- a) a reference to this International Standard;
- b) all details necessary for identification of the test sample;
- c) the drying time and temperature;
- d) the reduction time and temperature;
- e) the result obtained;
- f) all operations not specified in this International Standard, or regarded as optional;
- g) details of any occurrence which may have affected the result.

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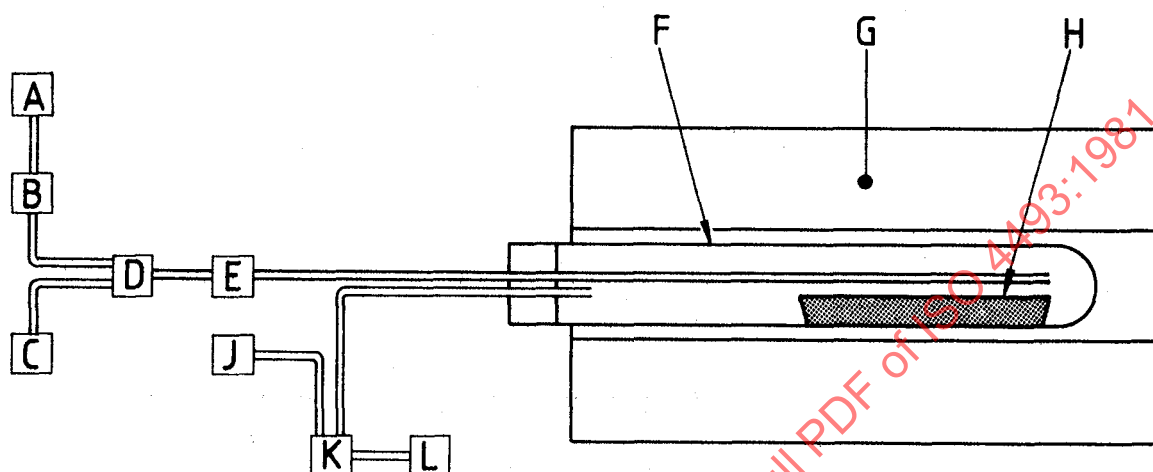


Figure 1 — Schematic arrangement of the apparatus

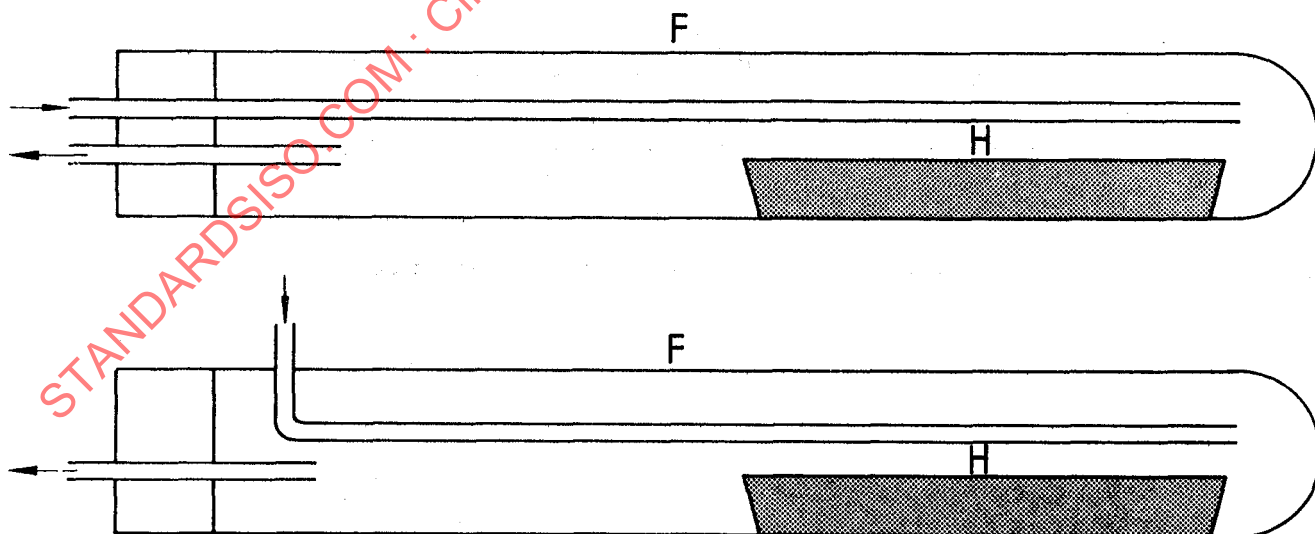


Figure 2 — Two examples of reduction tubes

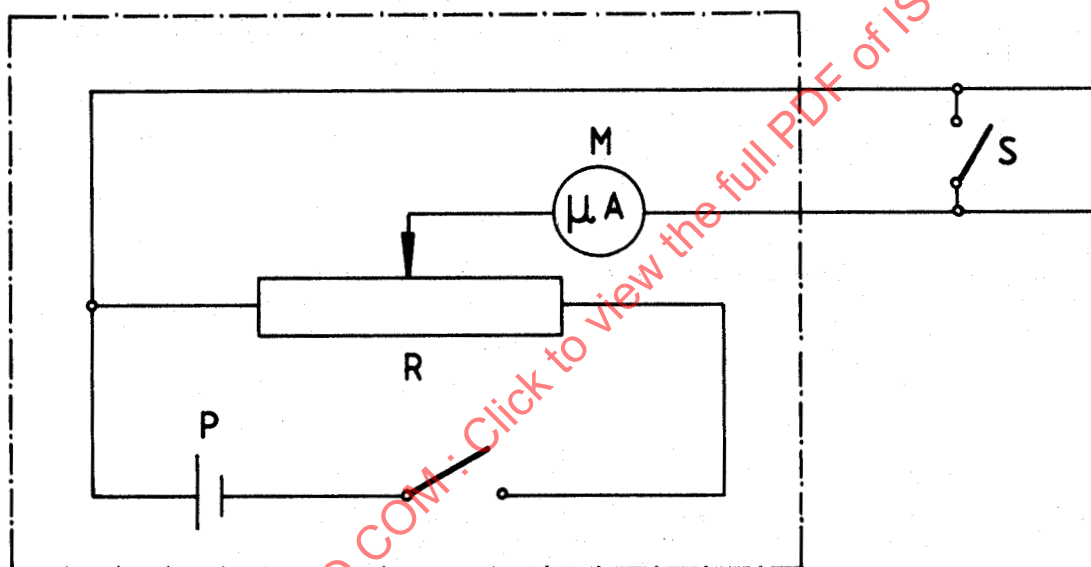


Figure 3 — Circuit diagram of an electrometric end-point detector



## Annex

### Notes and schematic representations of procedure

**A.1** The procedure with respect to temperature and time is shown diagrammatically in figure 4. During period  $t_1$ , the tube is purged with dry nitrogen at room temperature. At a flow rate of 15 l/h, 10 min are usually sufficient. During period  $t_2$ , the test portion is heated to 150 °C, ensuring the removal of moisture.

During period  $t_3$ , dry hydrogen is passed into the tube and the test portion is heated to the reduction temperature (900 or 1 100 °C).

During the period  $t_4$ , the test portion is cooled to room temperature under nitrogen.

Karl Fischer titrations are carried out after times  $t_1 + t_2$  (starting value) and  $t_1 + t_2 + t_3$ .

**A.2** The same procedure, but with respect to the collection of water in the Karl Fischer apparatus, and for the test portion (upper curve) and for the blank test (lower curve), is shown diagrammatically in figure 5.

During period  $t_1$ , the purging gas removes the moist atmospheric air in the tube and some of the adsorbed moisture on the test portion. When this is complete, the rate at which water enters the Karl Fischer apparatus is very small, indicated by angle  $\alpha$ . This corresponds to the residual moisture in the dry nitrogen and to minute diffusion arising from imperfect gas tightness. During period  $t_2$ , the moisture in the test portion is

completely removed, and, during period  $t'_2$ , the moisture flow rate falls again to that represented by angle  $\alpha$ .

During period  $t_3$ , water is produced by the reduction of the metal oxide, this being completed at the end of this period. During period  $t'_3$ , the moisture flow rate falls, corresponding to the residual oxygen and water in the hydrogen and to the leakage rate of the apparatus, which is indicated by angle  $\beta$ .

During period  $t_4$ , the value returns to that represented by angle  $\alpha$  as the hydrogen is replaced by nitrogen.

The values corresponding to the angles  $\alpha$  and  $\beta$  are established by the blank test, as shown in the lower curve.

The termination of drying (end of period  $t_2$ ) and the termination of reduction (end of period  $t_3$ ), shall be established by titration with the Karl Fischer reagent during periods  $t'_2$  and  $t'_3$  respectively. These latter periods shall be no longer than is necessary to ensure that drying and reduction are complete.

The titration result  $V_1$  corresponds to the reduction of the oxide in the test portion and the water derived from the imperfections indicated by angle  $\beta$ .

The titration result  $V_2$  corresponds to the water derived from the imperfection, angle  $\beta$ , determined in the blank test.

It is therefore important that the times and temperatures used in the blank test are the same as are used for the test portion.