INTERNATIONAL STANDARD

ISO 4491-3

Second edition
1997-04-01

Metallic powders — Determination of oxygen content by reduction methods —

Part 3:
Hydrogen-reducible oxygen

Poudres métalliques — Dosage de l'oxygène par les méthodes de réduction —

Partie 3: Oxygène réductible par l'hydrogène

Reference number
ISO 4491-3:1997(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4491-3 was prepared by Technical Committee ISO/TC 119, *Powder metallurgy*, Subcommittee SC 2, *Sampling and testing methods for powders (including powders for hardmetals)*.

This second edition cancels and replaces the first edition (ISO 4491-3:1989), clauses 7 and 8 of which have been technically revised.

ISO 4491 consists of the following parts, under the general title *Metallic powders — Determination of oxygen content by reduction methods*:

— *Part 1: General guidelines*

— *Part 2: Loss of mass on hydrogen reduction (hydrogen loss)*

— *Part 3: Hydrogen-reducible oxygen*

— *Part 4: Total oxygen by reduction-extraction*

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Introduction

The International Standard which the first edition of this part of ISO 4491 (ISO 4491-3:1989) replaced (ISO 4993:1981) described one particular arrangement of apparatus and procedure for the determination of hydrogen-reducible oxygen. However, it has since been established that other schemes will give equally valid results and these are therefore described in this part of ISO 4491.

In addition, the scope of the method has been extended to include powders containing carbon.

If carbon is present in the powder, some metal oxides which may otherwise have been reduced by hydrogen are instead reduced by carbon, producing carbon monoxide or carbon dioxide. These products are not measured by the titration with Karl Fischer reagent which is used to determine the amount of water produced. Consequently a lower result will be obtained for the hydrogen-reducible oxygen content.

This interference is eliminated by passing the gases emerging from the reduction furnace over a catalyst which converts the CO and CO_2 formed into methane and water, in accordance with the following equations:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The conversion reaction is carried out at 380 °C over a nickel catalyst.

NOTE — Certain oxides may be partially reduced by carbon which otherwise would not be reduced by hydrogen. In such cases the interpretation of results should be made with great care [see ISO 4491-1:1989, subclause 4.1.2 d)].

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Metallic powders — Determination of oxygen content by reduction methods —

Part 3:
Hydrogen-reducible oxygen

1 Scope

This part of ISO 4491 specifies a method for the determination of the hydrogen-reducible oxygen content of metallic powders containing 0,05 % (m/m) to 3 % (m/m) oxygen.

The method is applicable to unalloyed, partially alloyed or completely alloyed metal powders and also to mixtures of carbides and binder metal. It is not applicable to powders containing lubricants or organic binders.

The method may be extended to powders containing carbon by the use of a special catalytic device.

This part of ISO 4491 shall be read in conjunction with ISO 760 and ISO 4491-1.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 4491. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 4491 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 760:1978, *Determination of water — Karl Fischer method (General method).*

ISO 4491-1:1989, *Metallic powders — Determination of oxygen content by reduction methods — Part 1: General guidelines.*

3 Principle

Pre-treatment of a test portion by drying at low temperature (170 °C) in dry nitrogen or argon.

Reduction in a stream of pure dry hydrogen at a given temperature. Absorption in methanol of the water formed by reaction of oxides with hydrogen. Titration with Karl Fischer reagent, the end-point being determined either visually by the colour change or electrometrically with two electrodes (deadstop end-point).

For powders containing carbon, conversion of the carbon monoxide and carbon dioxide formed to methane and water at 380 °C by means of a nickel catalyst.

4 Reagents

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

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

4.1 Methanol, anhydrous.

4.2 Karl Fischer reagent, equivalent to 1 mg of oxygen per millilitre.

Determine the titre of the Karl Fischer reagent by one of the following methods:

a) Add to the titration flask 20 mg to 30 mg of water, weighed to the nearest 0,1 mg.

b) Add 100 mg to 200 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], previously ground to fine powder and dried at 105 °C ± 5 °C to constant mass.

c) Use the method described in clause 7, taking 100 mg to 200 mg of pure sodium tartrate dihydrate, weighed to the nearest 0,1 mg, as the test portion, but limiting the procedure to the drying step at 170 °C and the subsequent titration.

See ISO 760 for detailed procedures of standardization.

4.3 Hydrogen, having a maximum oxygen content of 0,005 % (*m*/*m*) and a dew point not exceeding – 45 °C.

4.4 Nitrogen or **argon**, having a maximum oxygen content of 0,005 % (*m*/*m*) and a dew point not exceeding – 45 °C.

4.5 Desiccant, consisting of granular anhydrous aluminium sodium silicate, activated silica gel or magnesium perchlorate.

5 Apparatus

NOTE — The alternative arrangements of the apparatus are shown in figure 1 (method 1) and figure 2 (method 2) respectively.

5.1 Hydrogen supply unit (A), fitted with a pressure-regulating valve, a flow control valve and a flow meter.

5.2 Purifier (B), for the hydrogen, containing a catalytic deoxidizer and a dryer.

5.3 Nitrogen (or **argon**) supply unit (C), fitted with a pressure-regulating valve, a flow control valve and a flow meter.

5.4 Gas-selection valve (D).

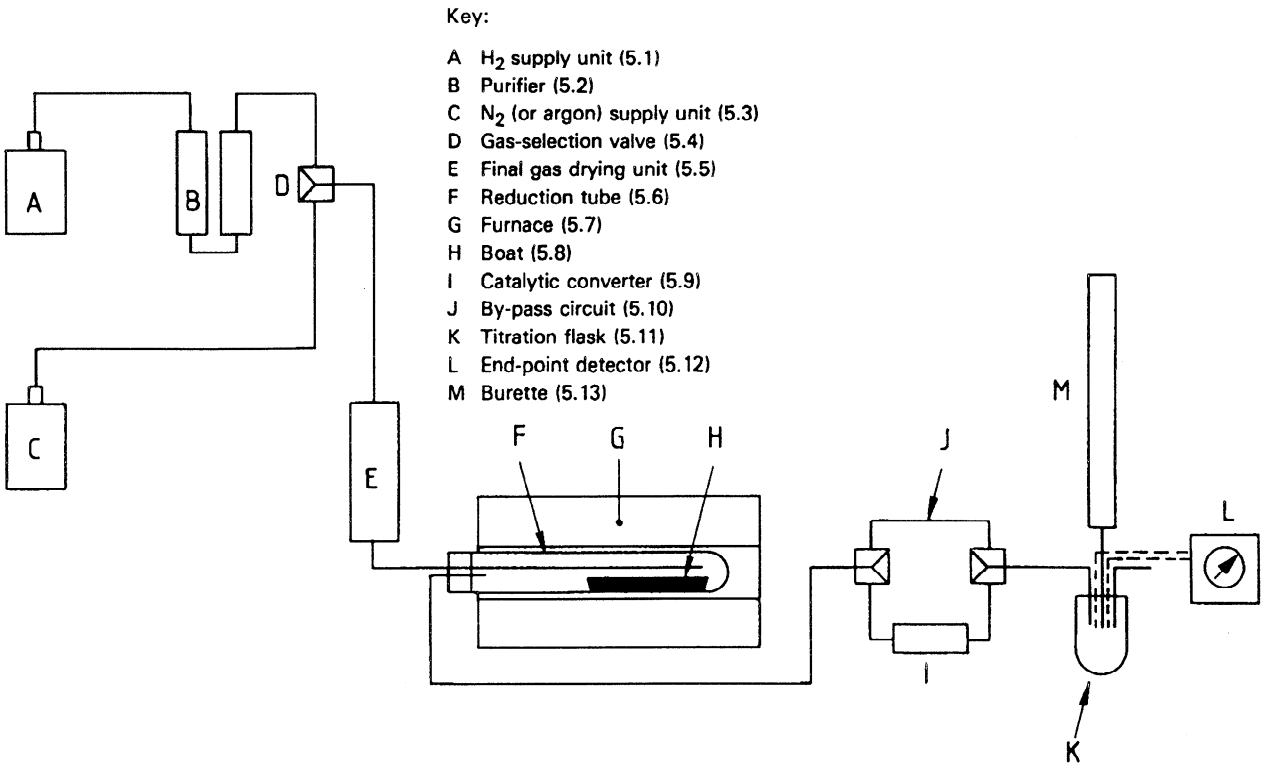


Figure 1 — Schematic arrangement of the apparatus for method 1

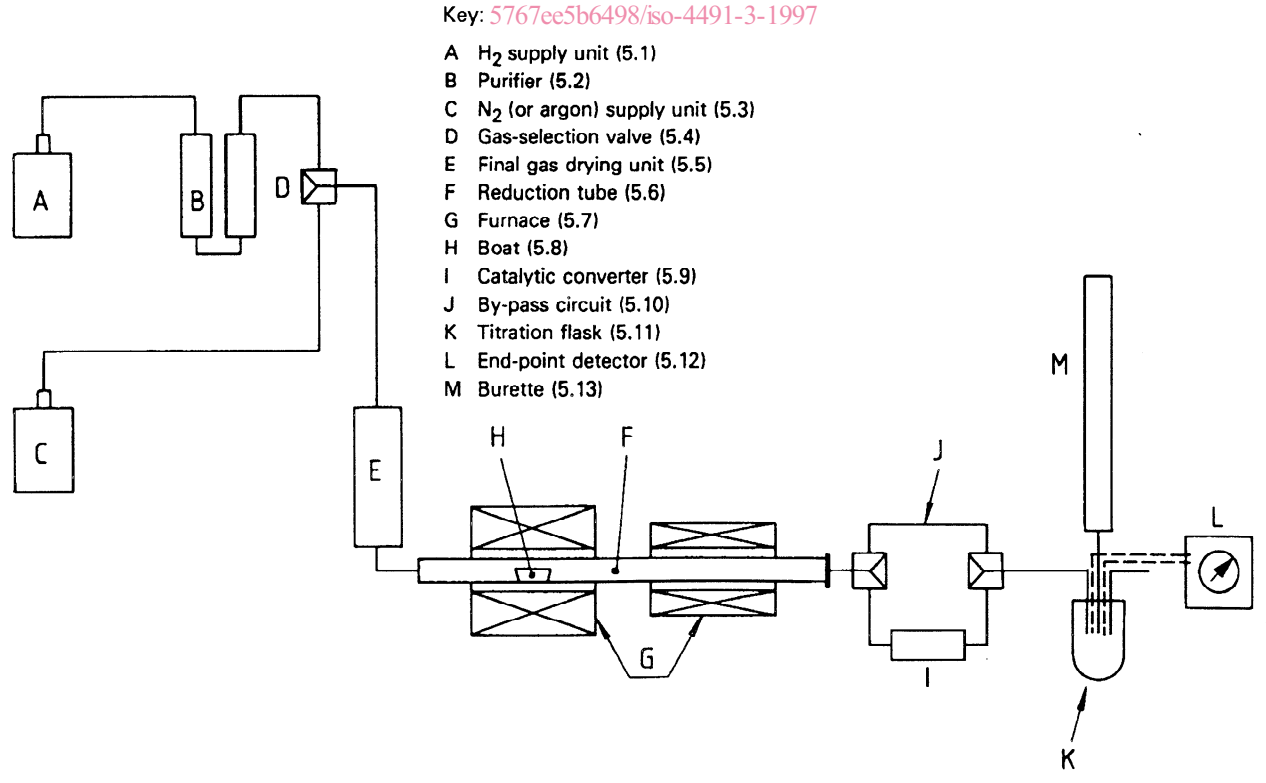


Figure 2 — Schematic arrangement of the apparatus for method 2

5.5 Final gas drying unit (E), containing desiccant (4.5).

5.6 Reduction tube (F), gas-tight, made of quartz or refractory material (for example dense alumina), meeting one of the following sets of specifications:

a) A tube closed at one end with an internal diameter of 27 mm to 30 mm and a length of about 400 mm with two smaller quartz tubes of diameter 5 mm to 6 mm and lengths 60 mm to 80 mm and 200 mm to 240 mm, respectively, arranged as shown in figure 3. This arrangement is inserted into the first drying furnace and then into the reduction furnace.

b) An open-ended tube with an internal diameter of about 20 mm, a length of 1 m, and a gas inlet and outlet. This tube is permanently inserted in the two furnaces.

5.7 Two furnaces (G), one for drying the test portion and the other for oxide reduction, with temperature control systems capable of maintaining the temperature in the part of the tube containing the boat (5.8) within the specified temperature tolerances.

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

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

5.9 Catalytic converter (I), comprising a glass tube filled with a nickel catalyst, and a furnace with temperature control system capable of maintaining the temperature in the glass tube at 380 °C. The catalyst shall be kept permanently under hydrogen.

5.10 By-pass circuit (J), used when the catalytic converter (5.9) is not needed, and designed so that air cannot reach the catalyst.

5.11 Titration flask (K), of capacity 200 ml to 300 ml, with magnetic stirrer or equivalent arrangement, equipped with two platinum electrodes if the end-point is to be detected electrometrically.

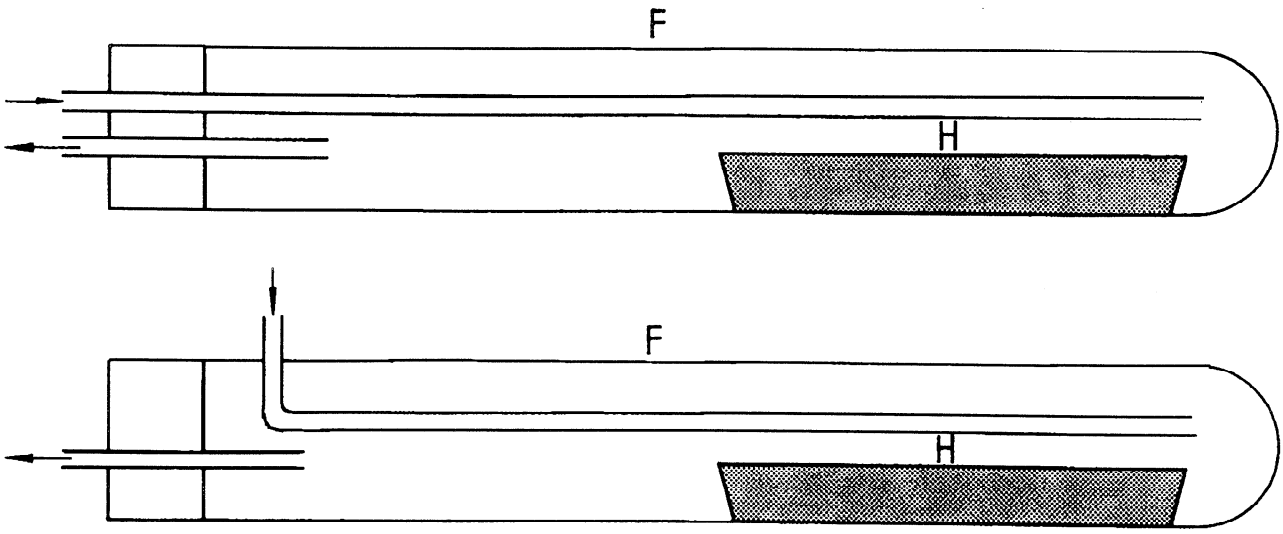
5.12 End-point detector (L), for use if the end-point is to be detected electrometrically. (See figure 4.)

5.13 Burette (M), of capacity 25 ml and with a fine tip graduated in 0,05 ml divisions, and protected from atmospheric moisture by a guard tube filled with desiccant (4.5).

The equipment described in 5.11, 5.12 and 5.13 may be modified, or any commercially available Karl Fischer, titration apparatus used, provided that the requirements of ISO 760 are fulfilled.

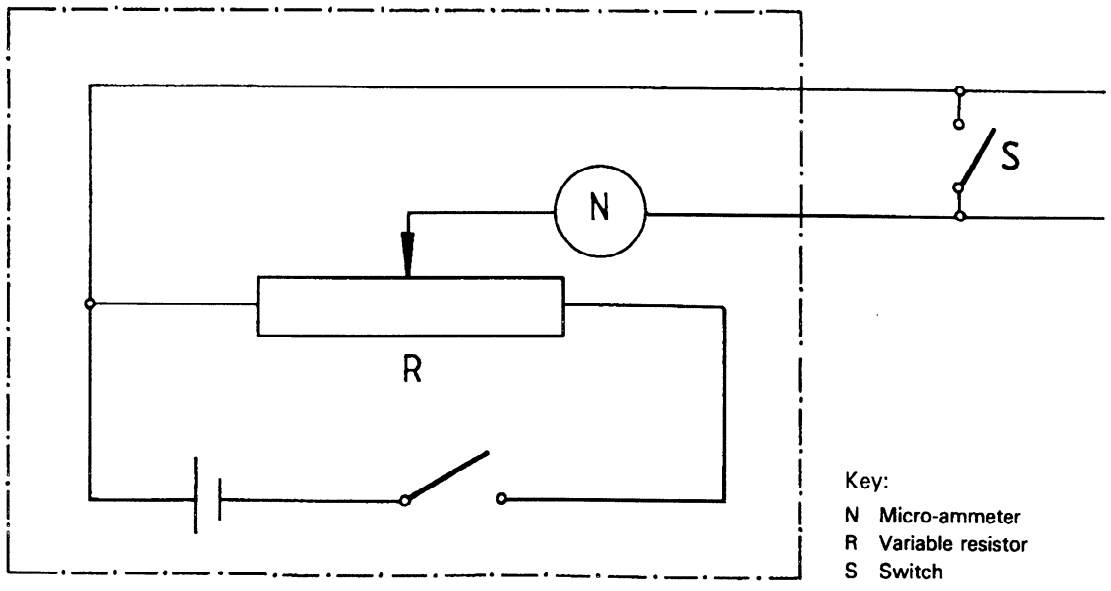
6 Sampling

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



Key:
F Reduction tube (5.6)
H Boat (5.8)

Figure 3 — Examples of reduction tubes



Key:
N Micro-ammeter
R Variable resistor
S Switch

Figure 4 — Schematic diagram of end-point detector L (see 7.3.4)