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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 : 1989 (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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4491-3 was prepared by Technical Committee ISO/TC 119, *Powder metallurgy.*

It cancels and replaces ISO 4493 : 1981, of which it constitutes a technical revision (see Introduction).

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 this part of ISO 4491 replaces (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, sub-clause 4.1.2 d)].

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.

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).

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

5.6 Reduction tube (F), gas-tight, made of quartz, 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.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,1 mg, a mass of test portion corresponding 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 given in table 2 are for guidance only and assume a reduction time of about 20 min.

Table 2

Metal powder	Reduction temperature °C
Iron and steel	1 000 ± 20
Nickel	900 ± 20
Cobalt	900 ± 20
Copper	900 ± 20
Molybdenum	1 100 ± 30
Tungsten	1 100 ± 30
Hardmetal mixture	900 ± 20

Key:

A H_2 supply unit (5.1)
B Purifier (5.2)
C N_2 (or argon) supply unit (5.3)
D Gas-selection valve (5.4)
E Final gas drying unit (5.5)
F Reduction tube (5.6)
G Furnace (5.7)
H Boat (5.8)
I Catalytic converter (5.9)
J By-pass circuit (5.10)
K Titration flask (5.11)
L End-point detector (5.12)
M Burette (5.13)

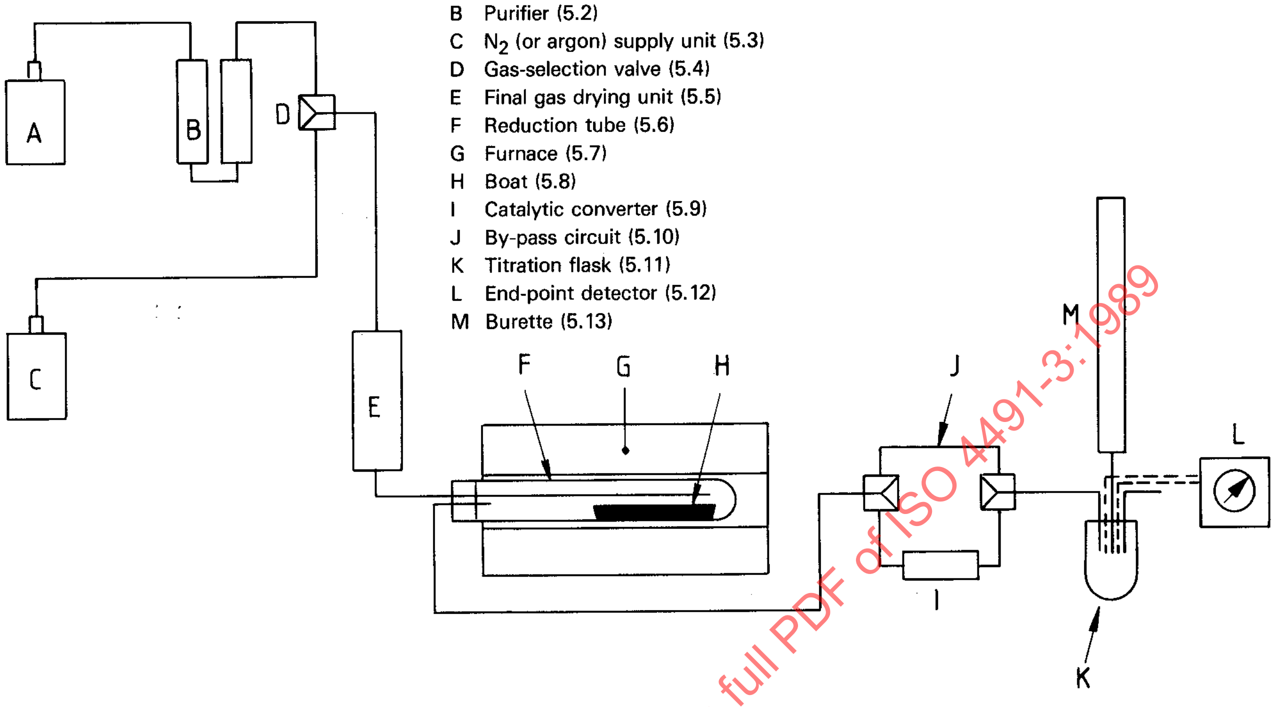


Figure 1 — Schematic arrangement of the apparatus for method 1

Key:

A H_2 supply unit (5.1)
B Purifier (5.2)
C N_2 (or argon) supply unit (5.3)
D Gas-selection valve (5.4)
E Final gas drying unit (5.5)
F Reduction tube (5.6)
G Furnace (5.7)
H Boat (5.8)
I Catalytic converter (5.9)
J By-pass circuit (5.10)
K Titration flask (5.11)
L End-point detector (5.12)
M Burette (5.13)

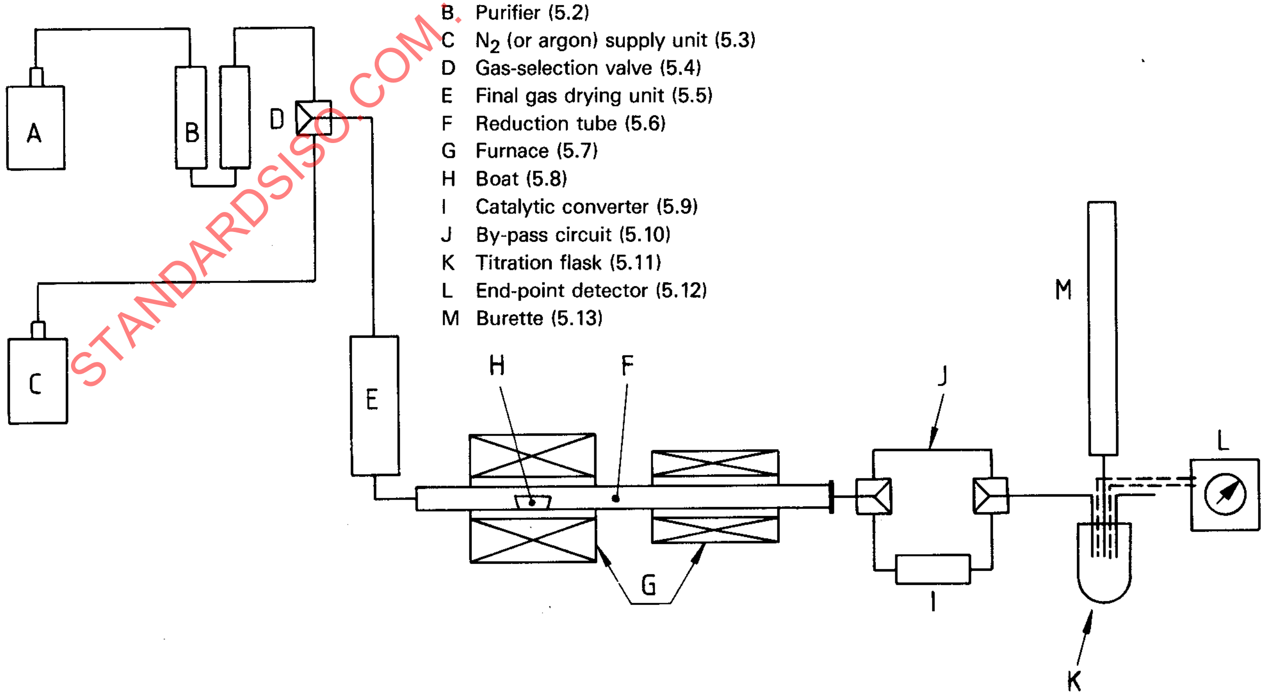
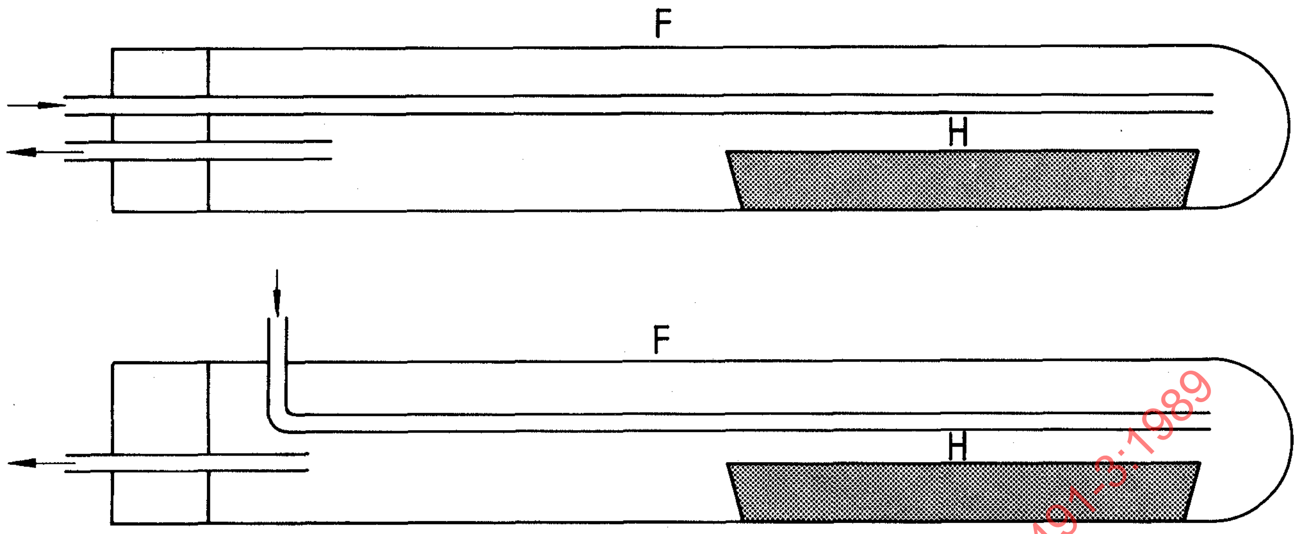


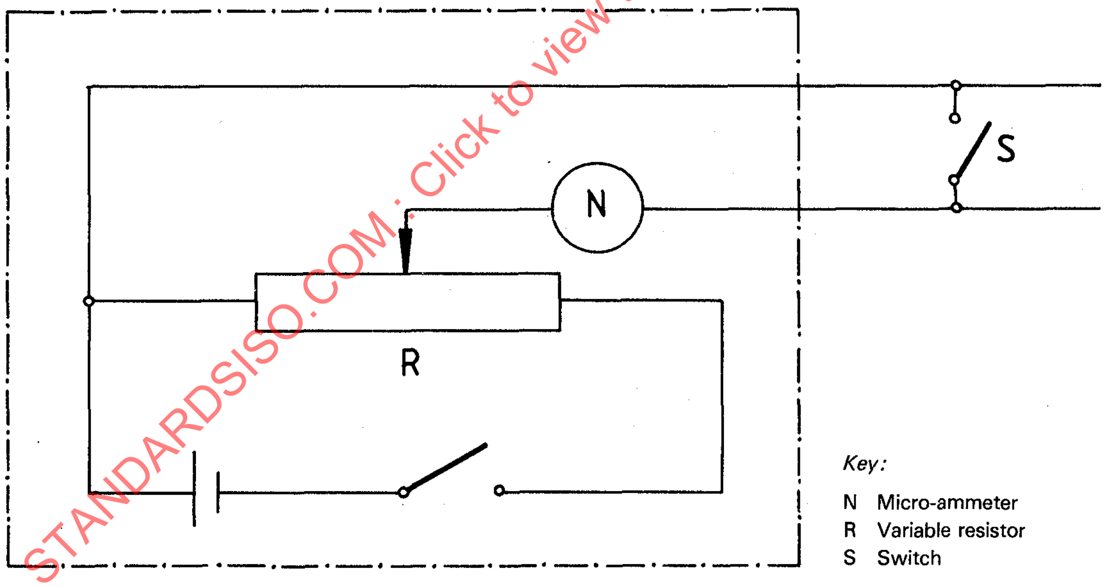
Figure 2 — Schematic arrangement of the apparatus for method 2



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)

Determine also the best drying time at 170 °C in dry nitrogen.

7.3 Preparation of the apparatus

7.3.1 Set up the apparatus as shown in figure 1 for method 1 or figure 2 for method 2. Set the temperature of the reduction furnace (see 5.7) to the reduction temperature. For method 1 only, leave the reduction tube [5.6 a)]outside the furnace.

7.3.2 Rinse the burette (5.13) with the Karl Fischer reagent (4.2) to ensure that no moisture, which could change the titre of the reagent, is present. Discard the rinsings and fill the burette with the Karl Fischer reagent.

7.3.3 Add the methanol (4.1) to the titration flask (5.11), taking care to adjust the liquid level so that the inlet tube (and the electrodes if used) are below the surface of the liquid. Start the 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 If electrometric end-point detection is used (see figure 4), short-circuit the electrodes by switch S of the electrometric end-point detector (5.12) and adjust the variable resistor R to give a current of 120 µA on the micro-ammeter N. Re-open switch S.

7.3.5 For both methods, adjust the nitrogen flow rate to at least 30 l/h and allow it to flow for 10 min. Change the gas flow from nitrogen to hydrogen by the gas-selection valve (5.4) and adjust the flow rate to about 25 l/h.

For method 1 only, insert the reduction tube [5.6 a)] in the reduction furnace and leave for 10 min. Change the gas flow back to nitrogen. Withdraw the tube and cool to room temperature.

7.3.6 Again titrate the methanol to the visual end-point to neutralize any traces of water released during conditioning.

7.3.7 Check the condition, including the gas-tightness, of the apparatus by the blank test specified in 7.4.

WARNING — Do not stop the hydrogen flow while the tube is still hot, except when changing back to nitrogen.

7.4 Blank test

For each series of determinations, carry out a blank test on an empty boat (5.8), following the same procedures as used for the test portion.

NOTE — An apparatus in good condition should 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 should be checked for leaks.

7.5 Determination

In both methods, if it is necessary to eliminate carbon interference, bring the catalytic converter (5.9) into operation by preheating it to 380 °C ± 10 °C and opening it to the system just before the boat is placed in the reduction zone.

At the end of the determination, ensure that the catalytic converter is by-passed before the hydrogen supply is changed to nitrogen.

NOTE — If required, the moisture content of the sample can be determined by recording the volume of Karl Fischer reagent used to titrate the water released during the drying period.

7.5.1 Method 1: Closed-end reduction tube

Open the reduction tube [5.6 a)] and insert the boat containing the weighed test portion. 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. Adjust the nitrogen flow to 25 l/h and insert the tube into the furnace at a temperature of 170 °C ± 10 °C. At the end of the drying period, titrate the methanol to the end-point, using either visual or electrometric end-point detection, having previously adjusted the detector as described in 7.3.4 if electrometric end-point detection is used. Record the volume of Karl Fischer reagent in the burette and the drying time. Using the gas-selection valve, change the gas flow from nitrogen to hydrogen, adjust the flow to 25 l/h and insert the tube into the reduction furnace maintained at the reduction temperature. At the end of the reduction period, titrate the methanol to the end-point using the same end-point determination as before. Read the burette and record the titrant volume V_1 in millilitres. Record the reduction time. 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, then open the tube and extract the boat.

7.5.2 Method 2: Open-ended reduction tube

Ensure that the furnace temperatures are set correctly. Purge with dry nitrogen and then open the reduction tube [5.6 b)] and insert the boat containing the test portion. Using a stainless steel hook, push the boat into the drying zone and close the tube with a gas-tight seal. At the end of the drying period, titrate the methanol with Karl Fischer reagent.

Change the gas from nitrogen to hydrogen and push the boat into the high-temperature zone of the reduction furnace. At the end of the reduction period titrate with Karl Fischer reagent. Record the volume V_1, in millilitres, of reagent used.

Change the gas from hydrogen to nitrogen. Move the boat to the low-temperature zone and after 1 min remove it from the tube.

7.6 Carry out the determination at least in duplicate.

8 Expression of results

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

$$O_{red} = 100\, n \frac{V_1 - V_2}{m}$$