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Metallic powders — Determination of oxygen content by reduction methods —

Part 1: General guidelines

*Poudres métalliques — Dosage de l'oxygène par les méthodes de
réduction —
Partie 1: Directives générales*

[ISO/FDIS 4491-1](https://standards.iso.org/iso-fdis-4491-1)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 119, *Powder metallurgy*, Subcommittee SC 2, *Sampling and testing methods for powders (including powders for hardmetals)*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/SS M11, *Powder metallurgy*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 4491-1:1989), of which it constitutes a minor revision.

The main changes are as follows:

- the normative references in [Clause 2](#) have been updated;
- [Clause 6](#) and [7](#) have changed place;
- editorial corrections and updated ISO format have been applied.

A list of all parts in the ISO 4491 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

In powder metallurgy, the purity of the powders is an important parameter for the manufacture of sintered metals. Among the various impurities which may be present in a powder, oxygen plays a particular role as it is always present in any metal or alloy powder, and in amounts greater than those encountered in compact metals. Oxygen is mostly combined in the form of oxides which appear in the following ways:

- Oxide film coatings on particle surfaces, spontaneously formed by oxidation of the metal by air or moisture during powder preparation and during handling and storage.
- Oxide inclusions, being either oxides of the main metal remaining locally unreduced during the production process (in the case of reduced powders), or other oxide impurities originating from the raw material and/or from the equipment (e.g. refractory ceramics from melting furnace in atomization processes).

In practice, oxygen contents in metallic powders lie mostly in the range of a mass fraction of 0,1 % to a mass fraction of 1 %.

The determination of oxygen content can be made by means of many physical or chemical methods, for example:

- a) specific methods, such as activation analysis or mass spectrometry, in which the element O is directly determined;
- b) reduction methods, in which oxides present are, totally or partially, reduced by hydrogen or by carbon. Oxygen content is related, either to the loss of mass of the sample through reduction, or to the amount of water or CO/CO₂ produced by the reaction;
- c) separation methods, in which:
 - either the oxide phase is selectively dissolved and determined chemically (for example in copper powder, where copper oxide is dissolved by hydrochloric acid); or
 - the metal phase is selectively dissolved, and the insoluble residue (assumed to be oxide) is evaluated (for example in aluminium powder, aluminium is dissolved in bromine-methanol reagent, leaving aluminium oxide).

The document considers only reduction methods, as these are commonly used in laboratories for analysing a great variety of metal powders.

Metallic powders — Determination of oxygen content by reduction methods —

Part 1: General guidelines

1 Scope

This document is the first part of a series of standards dealing with the determination of oxygen content in metallic powders by reduction methods. It specifies general guidance to these methods and gives some recommendations for the correct interpretation of the results obtained.

The test methods are applicable generally to all powders of metals, alloys, carbides and mixtures thereof. The constituents of the powder shall be non-volatile under the conditions of test. The powder shall be free of lubricant or organic binder.

However, there exist certain limitations which depend upon the nature of the analysed metal. These limitations are discussed in Clause 4.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3954, *Powders for powder metallurgical purposes — Sampling*

ISO 4491-2, *Metallic powders - Determination of oxygen content by reduction methods - Part 2: Loss of mass on hydrogen reduction (hydrogen loss)*

ISO 4491-3, *Metallic powders — Determination of oxygen content by reduction methods — Part 3: Hydrogen-reducible oxygen*

ISO 4491-4, *Metallic powders — Determination of oxygen content by reduction methods — Part 4: Total oxygen by reduction-extraction*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Sampling

For sampling of the powder, the procedures in ISO 3954 shall be used.

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

Metallic powders are frequently reactive substances with respect to air and moisture. Therefore, particular attention shall be given to adequate conditions for handling and storage of the test sample. The test portion shall be taken immediately prior to the analysis.

5 Meaning of the results according to the method used

5.1 Hydrogen as a reducing agent

5.1.1 At the test temperatures prescribed in the determination, only the following metals have oxides totally reducible by hydrogen:

Fe, Ni, Co, Cu, Ag, Sn, Pb, W, Mo, Re

All other common oxides are not reducible, in particular Al_2O_3 , SiO_2 , ZrO_2 and other oxides of alkali, alkali-earth and most rare-earth metals. Oxides of chromium, manganese, titanium, and vanadium may be partially reducible.

5.1.2 However, other reactions with constituents of the powder take place during the reduction process.

- a) Water vapour and/ or hydrocarbons present in the sample, and also gases, which possibly by adsorption or occlusion are contained in the powder, are released during heating.
- b) Elements, such as carbon, nitrogen, sulphur, phosphorus, free or combined in the powder, may be completely or partially removed, either because they are volatile or because they react with hydrogen or with oxides in the powder, forming volatile compounds.
- c) Some metals present in the powder, such as lead, tin, cadmium, zinc, may be partially or completely volatilized, depending on the test conditions.
- d) Carbon present in the powder can also reduce oxides under the specified test conditions, and possibly also oxides that normally are not reduced or are only partially reduced by hydrogen, such as chromium, manganese and vanadium oxides.
- e) Alloy powders containing metallic elements with high affinity for oxygen, such as chromium, manganese, silicon, aluminium and titanium, may be oxidized during the test by reaction with the atmosphere or with less refractory oxides, entailing an apparent decrease of measured oxygen content.

5.1.3 The loss of hydrogen method in ISO 4491-2, the loss of mass of the test portion, when submitted to a specified heat treatment in hydrogen, is measured. Originally this test was considered to give an estimate of the oxygen content of a metal powder, the oxide of which is reducible by hydrogen. However, with the advent of more complex or alloyed powders, all the reactions considered in 5.1.2 may contribute, positively or negatively, to the measured loss of mass. Therefore, this test method is purely conventional, and its reproducibility requires a scrupulous respect of the operating procedure. This method is commonly used in routine control of powders of certain defined metals in accordance with ISO 4491-2.

5.1.4 The method of determination oxygen emanating from hydrogen-reducible oxides in accordance with ISO 4491-3, the quantity of water formed by hydrogen reduction of these oxides is measured by titration. In comparison with the loss in hydrogen method, this method is more specific for the following reasons:

- The interference of moisture and adsorbed gases is prevented by pre-treatment at low temperature. With a slight modification of the procedure, it is possible to determine the water content of the sample

- The interference of metalloids and of volatile metals is avoided.

However, interference of carbon present in the sample may have to be taken into account. Some part of the metal oxides, which otherwise may have been reduced by hydrogen, are reduced by carbon, producing carbon monoxide or dioxide, which are not measured by water titration. Consequently, a lower result will be obtained. Therefore, two alternative methods are specified:

- Method 1: Oxygen content corresponding to hydrogen-reducible oxides, without taking into account carbon interference. This method is applicable in practice when the sampled powder is known to be almost free of carbon [for example $C < 0,02\%$ (m/m) or the carbon present is in an unreactive form. Then the result represents the oxygen content from hydrogen-reducible oxides
- Method 2: Oxygen content corresponding to hydrogen-reducible oxides, taking into account carbon interference. In this method the $CO + CO_2$ gases released by carbon reduction of some of the oxides and contained in the H_2 carrier gas, are quantitatively converted to methane and water on a nickel catalyst at $380\text{ }^\circ\text{C}$. The total water determined represents the oxygen content emanating from hydrogen-reducible oxides, irrespective of whether the actual reduction has taken place by means of hydrogen or carbon.

With reference to 5.1.2 d), certain oxides can be partially reduced by carbon, i.e. oxides which otherwise would not be reduced by hydrogen. In such a case, the test conditions shall be subject to a special agreement and interpretation of the result should be made with great care.

5.2 Carbon as a reducing agent: reduction extraction method

The method in accordance with ISO 4491-4 is based on the reduction of the sample by graphite at very high temperature, ($2\ 000\text{ }^\circ\text{C}$ to $3\ 000\text{ }^\circ\text{C}$), either under vacuum or in a flow of pure inert gas (for example argon). Depending on the metal analysed, the operating conditions are chosen so that all the oxides, even the most refractory ones, are reduced totally. Any interference is completely excluded, and the result represents accurately the total oxygen content of the sample.

6 Summary of the implementation of methods for oxygen determination by reduction

Two cases are considered,

- Metals of oxides which are reducible by hydrogen ("H reducible") and which possibly contain carbon, for example:

Fe, Ni, Co, Cu, Ag, Sn, Pb, W, Mo, Re

When such a metal is reduced by hydrogen, the behaviour of the oxygen and carbon content is represented by the analytical results according to [Table 1](#).

Table 1 — Representation of analytical results when metals of oxides are reduced by hydrogen

Content of oxygen	contained in hydrogen reduced oxides	O_H
	contained in carbon reduced oxides	O_C
	from remaining (unreduced) oxides	O_r
Content of carbon having reacted		C_0

- Any metal (containing carbon or not)

When reduced totally by graphite (reduction-extraction method), the total oxygen content, O_t , is measured.

7 Practical application of the standard methods

Table 2 gives a summary of the applicable methods, depending on the type of powder analysed and on the nature of the oxygen which shall be determined. It should be emphasized that a combination of several methods can bring precise information, for example:

- on the "hydrogen-reducible" and "hydrogen-irreducible" oxygen, i.e. the presence of refractory oxides in "hydrogen-reducible" metals;
- on the internal effect of carbon, when present, on the reduction of oxides.

An interesting alternative is to carry out the total oxygen determination on a test portion already reduced by hydrogen (by means of a loss in hydrogen test or a hydrogen-reducible oxygen test). In this way, the content of oxygen not reduced by hydrogen (and by internal carbon) under the conditions of hydrogen reduction can be determined.

Table 2 — Content determined depending on method used

Powder	Method				
	Hydrogen loss	Hydrogen-reducible oxygen		Reduction-extraction	
		Direct method	With correction for carbon	On initial sample	On sample reduced by hydrogen
Metals with Hydrogen reducible oxides:					
Not containing carbon	O_H	O_H	O_H	$O_t = O_H + O_r$	O_r
Containing carbon	$O_H + O_C + C_O$	O_H	$O_H + O_C$	$O_t = O_H + O_C + O_r$	O_r
Any other metal				O_t	

NOTE - In this table, interference by moisture, adsorbed gases, volatile and reoxidizable metals, is assumed to be absent.