# INTERNATIONAL STANDARD

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# Hydrogen fuel — Product specification

Carburant hydrogène — Spécification de produit



# ISO 14687:1999(E)

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#### **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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

This document was prepared by Technical Committee ISO/TC 197, Hydrogen technologies.

# **Hydrogen fuel** — Product specification

# 1 Scope

This International Standard specifies the quality characteristics of hydrogen fuel in order to assure uniformity of the hydrogen product as produced and distributed for utilization in vehicular, appliance or other fuelling applications.

This International Standard applies to all modes of transportation and hydrogen fuelling applications (ground, water, air and space).

#### 2 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

#### 2.1

#### gaseous hydrogen

#### $GH_2$

hydrogen that has been produced to gaseous form, and brought to essentially ambient conditions as an equilibrium mixture of *ortho*-hydrogen and *para*-hydrogen, purified to a minimum mole fraction of 98 %

NOTE The gaseous form is produced typically by any number of methods, including petrochemical, thermochemical, solar, electrolytic or biological processes.

#### 2.2

#### liquid hydrogen

#### LH<sub>2</sub>

hydrogen that has been liquefied, i.e. brought to a liquid state (para)

NOTE Liquefaction may be carried out by either chilling and compression or other means such as the magnetocaloric effect.

#### 2.3

#### slush hydrogen

# SLH<sub>2</sub>

hydrogen that is a mixture of solid and LH<sub>2</sub> at the eutectic (triple-point) temperature

### 3 Requirements

#### 3.1 Classification

Hydrogen fuel shall be classified according to the following types and grade designations:

a) Type I (grades A, B, and C): Gaseous hydrogen

b) Type II: Liquid hydrogen

c) Type III: Slush hydrogen

# 3.2 Applications

The following information characterizes representative applications of each type and grade of hydrogen fuel. It is noted that suppliers (especially liquid transporters) commonly transport hydrogen of a higher quality than some users may require. The "lower" grades A and B entail less stringent requirements, which may be more suitable for "captive" systems such as vehicle fleets/common fill or on-site hydrogen production/use, such as in industrial complexes.

Type I, grade A internal combustion engines/fuel cells for transportation; residential/commercial appliances;

Type I, grade B industrial fuel, for use e.g. in power generation or as a heat energy source;

Type I, grade C aircraft and space-vehicle ground support systems;

Type II aircraft and space-vehicle onboard propulsion and electrical energy requirements; land vehicles;

Type III aircraft and space-vehicle onboard propulsion.

# 3.3 Limiting characteristics

The Directory of Limiting Characteristics, outlined in Table 1, specifies the requirements applicable to each type and grade of hydrogen fuel. A blank indicates no maximum limiting characteristic. The absence of a maximum limiting characteristic in a listed quality level does not imply that the component is or is not present, but merely indicates that the test need not be performed for compliance with this International Standard.

# 4 Quality verification

### 4.1 Quality tests

The supplier shall assure, by standard practice, the verification of the quality level of hydrogen. The sampling and control procedures described in 4.3.1 and 4.3.2 and in clauses 5 and 6 may be applied. Other control procedures not listed in this International Standard are acceptable if agreed upon between the supplier and the customer.

#### 4.2 Production qualification tests

#### 4.2.1 General requirements

Production qualification tests are a single analysis or a series of analyses that shall be performed on the product to assure the reliability of the production facility to supply hydrogen of the required quality level. This production qualification may be achieved by verifying the analytical records of product from the supplier, or, if required, by performing analyses of representative samples of the product from the facility at appropriate intervals as agreed between the supplier and the customer. Production qualification tests may be performed by the supplier or by a laboratory agreed upon between the supplier and the customer.

#### 4.2.2 Analytical requirements of the production qualification tests

The analytical requirements for the production qualification tests shall include the determination of all limiting characteristics of hydrogen.

Table 1 — Directory of limiting characteristics

Dimensions in micromoles per mole unless otherwise stated

Subclause	Characteristics	Type I			Type II	Type III
	(assay)	Grade A	Grade B	Grade C		
6.2	Hydrogen purity (minimum mole fraction, %)	98,0	99,90	99,995	99,995	99,995
6.3	Para-hydrogen (minimum mole fraction, %)	NS	NS	NS	95,0	95,0
	Impurities (maximum content)					
	Total gases			50	50	
6.4	Water (cm <sup>3</sup> /m <sup>3</sup> )	NC <sup>a</sup>	NC	b	b	
6.5	Total hydrocarbon	100	NC	b	b	
6.6	Oxygen	а	100	С	С	
6.7	Argon	а		С	С	
6.7	Nitrogen	а	400	b	b	
6.7	Helium			39	39	
6.8	CO <sub>2</sub>			d	d	
6.9	СО	1		d	d	
6.10	Mercury		0,004			
6.11	Sulfur	2,0	10			
6.12	Permanent particulates	f	е	е	е	
	Density					е

NOTE 1 NS: Not specified

NOTE 2 NC: Not to be condensed

 $<sup>^{\</sup>text{a}}$  Combined water, oxygen, nitrogen and argon: max. 1 900  $\mu\text{mol/mol}.$ 

<sup>&</sup>lt;sup>b</sup> Combined nitrogen, water and hydrocarbon: max. 9 μmol/mol.

 $<sup>^{\</sup>text{C}}$  Combined oxygen and argon: max. 1  $\mu\text{mol/mol.}$ 

 $<sup>^{\</sup>mbox{\scriptsize d}}$  Total  $\mbox{CO}_2$  and CO: max. 1  $\mu\mbox{mol/mol}.$ 

<sup>&</sup>lt;sup>e</sup> To be agreed between supplier and customer.

f The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to damage the fuelling station equipment or the vehicle (engine) being fuelled.

#### 4.3 Lot acceptance tests

#### 4.3.1 Applicability

Lot acceptance tests are analyses that shall be performed on the hydrogen in the delivery container, or a sample thereof, which is representative of the lot.

#### 4.3.2 Lot definitions

One of the following definitions of the lot shall be used:

- a) no specific quantity, or any quantity of hydrogen agreed upon between the supplier and the customer;
- b) all of the hydrogen supplied, or containers filled, during the contract period;
- c) all of the hydrogen supplied, or containers filled, during a calendar month;
- d) all of the hydrogen supplied, or containers filled, during seven consecutive days;
- e) all of the hydrogen supplied, or containers filled, during a consecutive 24-h period;
- f) all of the hydrogen supplied, or containers filled, during one continuous shift;
- g) all of the hydrogen supplied in one shipment;
- h) all of the hydrogen supplied in one delivery container;
- i) all of the hydrogen in the container(s) filled on one manifold at the same time.

#### 4.3.3 Number of samples per lot

The number of samples per lot shall be in accordance with one of the following:

- a) one sample per lot;
- b) any number of samples agreed upon by the supplier and the customer.

# 5 Sampling

#### 5.1 Sample size

The quantity of hydrogen in a single sample container shall be sufficient to perform the analyses for the limiting characteristics. If a single sample does not contain a sufficient quantity of hydrogen to perform all of the analyses required to assess the quality level, additional samples from the same lot shall be taken under similar conditions.

#### 5.2 Gaseous samples

Gaseous samples shall be representative of the hydrogen supply. Samples shall be obtained using one of the following procedures.

- a) Fill the sample container and delivery containers at the same time, on the same manifold and in the same manner.
- b) Withdraw a sample from the supply container through a suitable connection into the sample container. No regulator shall be used between the supply and the sample containers (a suitable purge valve may be used).

For safety reasons, the sample container and sampling system shall have a rated service pressure at least equal to the pressure in the supply container.

c) Connect the container being sampled directly to the analytical equipment using suitable pressure regulation to prevent over-pressurizing this equipment.

d) Select a representative container from the containers filled in the lot.

#### 5.3 Liquid samples (vaporized)

Vaporized liquid samples shall be representative of the liquid hydrogen supply. Samples shall be obtained using one of the following procedures:

- a) by vaporizing, in the sampling line, liquid hydrogen from the supply container;
- b) by flowing liquid hydrogen from the supply container into or through a suitable container in which a representative sample is collected and then vaporized.

#### 6 Test methods

### 6.1 Parameters of analysis

The parameters for analytical techniques contained in this clause are:

- a) mole fraction, expressed as a percentage (%);
- b) number of cubic centimetres per cubic metre (cm<sup>3</sup>/m<sup>3</sup>) [water only];
  - NOTE 1 Contents in 6.1 a) and b) represent  $10^{-6}$ .
- c) number of micromoles per mole (μmol/mol).

Total hydrocarbon content "as methane" for the purpose of this International Standard is defined as the single carbon atom equivalent.

Calibration gas standards which contain the applicable gaseous components may be needed to calibrate the analytical instruments used to determine the limiting characteristics of hydrogen.

If required by the customer, the accuracy of the measuring equipment used in preparing these standards shall be traceable to an established institute for standards.

Analytical equipment shall be operated in accordance with the manufacturer's instructions.

Analytical methods not listed in this International Standard are acceptable if agreed upon between supplier and customer.

# 6.2 Hydrogen assay for purity

The hydrogen concentration shall be determined by one of the following procedures.

- a) Use a thermal conductivity analyser which measures the aggregate impurities which have thermal conductivities different from hydrogen. The analyser shall be calibrated at appropriate intervals using calibration gas standards. The range of the analyser shall be no greater than ten times the difference between the specified minimum hydrogen concentration, in percent, and 100 %. Thus for a 99,5 % minimum hydrogen concentration, the analyser shall have a maximum range of 5 % impurity or from 95 % to 100 % hydrogen.
- b) Use a volumetric or manometric gas analysis apparatus.
- c) Determine the amount of aggregate impurities using the methods in the following subclauses of this International Standard. The hydrogen concentration is the value obtained when this amount, expressed as percent mole fraction, is subtracted from 100 %.
- d) Use any suitable chromatographic system which effectively quantifies specific impurities [see 6.7 a)].

# 6.3 Hydrogen assay for para-hydrogen

Para-hydrogen (percent minimum balance *ortho*-hydrogen) shall be determined using thermal conductivity-type instream analysers installed in the supplier's production system and shall be calibrated integrally by the appropriate use of temperature-controlled catalyst beds.

NOTE Industrial users of hydrogen typically do not require lot analysis for *para* content. The test may be performed as agreed upon between the supplier and the customer.

#### 6.4 Water content

The water content shall be determined using one of the following procedures.

a) Support the hydrogen cylinder in an inverted position (valve at the bottom) for 5 min. Then open the cylinder valve slightly while the cylinder remains inverted, and vent the hydrogen with a barely audible flow into an open, dry container for 1 min.

The cylinder and its content shall be above 0 °C. This procedure shall not be used for hydrogen fuel other than Type I, grades A and B. This procedure detects condensed hydrocarbons (oil) as well as water.

NOTE A rapid flow may cause any water to disperse and not collect in the container.

- b) Use an electrolytic hygrometer having an indicator graduated in cubic centimetres per cubic metre on a range which is no greater than ten times the specified maximum water content. Recombination of oxygen with hydrogen can occur, producing a false high reading; refer to instrument manufacturer's instructions for proper analytical technique.
  - NOTE Recombination of oxygen with hydrogen can occur, producing a false high reading. Refer to instrument manufacturer's instructions for proper analytical technique.
- c) Use a dewpoint analyser in which the temperature of a viewed surface is measured at the time moisture first begins to form.
- d) Use a piezoelectric (e.g. vibrating-quartz) absorption hygrometer, of which the accuracy of analysis shall be  $\pm 0.1 \text{ cm}^3 \cdot \text{m}^{-3}$  or 5 % of the reading, whichever is greater.
- e) Use a metal oxide capacitor-equipped analyser on a range which is no greater than ten times the specified maximum water content.

#### 6.5 Total hydrocarbon content

The total (volatile) hydrocarbon content (as methane) shall be determined using one of the following instruments.

- a) Use a flame ionization-type analyser, calibrated at appropriate intervals by the use of calibration gas standards. The range used shall be no greater than ten times the specified maximum total hydrocarbon content expressed as methane.
- b) Use a gas-cell-equipped infrared analyser, calibrated at appropriate intervals by use of calibration gas standards at a wavelength of approximately 3,5 μm (the characteristic absorption wavelength for C—H stretching). The analyser shall be operated so that its sensitivity for methane is at least 0,1 μmol·mol<sup>-1</sup> or 10 % of the specified maximum total hydrocarbon content, whichever is greater.

# 6.6 Oxygen content

The oxygen content shall be determined using one of the following instruments.

a) Use an electrochemical-type oxygen analyser containing a solid or an aqueous electrolyte and calibrated at appropriate intervals by use of calibration gas standards or integrally in accordance with Faraday's Law. The range used shall be no greater than ten times the specified maximum oxygen content.

b) Use a heat-of-reaction-type analyser, calibrated at appropriate intervals by the use of calibration gas standards, or integrally in accordance with Faraday's Law. The range used shall be no greater than ten times the specified maximum oxygen content.

- c) Use an analyser in which oxygen reacts to form a compound which is subsequently measured. The analyser shall be calibrated at appropriate intervals by the use of calibration gas standards. The range used shall be no greater than ten times the specified maximum oxygen content.
- d) Use a gas chromatograph such as that described in 6.7 a).
- e) Use a mass spectrometer, operated so that its sensitivity is at least  $0.5 \, \mu \text{mol} \cdot \text{mol}^{-1}$  or 10 % of the specified maximum oxygen content, whichever is greater.

# 6.7 Argon, nitrogen, neon and helium contents

The argon, nitrogen, neon and helium contents shall be determined using one of the following instruments.

- a) Use a gas chromatograph, capable of separating and detecting the desired component with a sensitivity of 0,5 μmol·mol<sup>-1</sup> or 20 % of the specified maximum content of the component, whichever is greater. Appropriate impurity-concentrating techniques may be used to attain the sensitivity. The analyser shall be calibrated at appropriate intervals by the use of calibration gas standards.
  - NOTE This method may be used not only for argon, nitrogen, neon and helium determinations, but also for the determination of any other limiting characteristic of gaseous components.
- b) Use a mass spectrometer, operated so that its sensitivity is at least  $0.5 \, \mu \text{mol} \cdot \text{mol}^{-1}$  or 10 % of the specified maximum content of the component, whichever is greater.

#### 6.8 Carbon dioxide content

The carbon dioxide content shall be determined using one of the following instruments.

- a) Use a gas-cell-equipped infrared analyser. The analyser shall be calibrated at appropriate intervals by the use of calibration gas standards at a wavelength of approximately 4,3  $\mu$ m. The analyser shall be operated so its sensitivity for carbon dioxide is at least 0,1  $\mu$ mol·mol<sup>-1</sup> or 10 % of the specified maximum carbon dioxide content, whichever is greater.
- b) Use a gas chromatograph such as that described in 6.7 a). The technique utilized shall be specific for the separation and analysis of carbon dioxide.
- c) Use a catalytic methanator gas chromatograph such as that described in 6.7 a).
- d) Use an analyser in which carbon dioxide reacts to form a compound which is subsequently measured. The analyser shall be calibrated at appropriate intervals by the use of calibration standards. The range used shall be no greater than ten times the specified maximum carbon dioxide content.

## 6.9 Carbon monoxide content

The carbon monoxide content shall be determined using one of the following instruments.

- a) Use an apparatus employing a detector tube filled with a colour-reactive chemical. The degree of accuracy is dependent on the precision of the measurements and analytical bias of the tube.
- b) Use a gas-cell-equipped infrared analyser, calibrated at appropriate intervals by the use of calibration gas standards at approximately 4,6  $\mu$ m. The analyser shall be operated so that its sensitivity for carbon monoxide is at least 0,1  $\mu$ mol  $\cdot$  mol<sup>-1</sup>, or 10 % of the specified maximum carbon monoxide content, whichever is greater.
- c) Use an analyser in which carbon monoxide reacts to form a compound whose content is subsequently measured. The analyser shall be calibrated at appropriate intervals by the use of calibration standards. The range used shall be no greater than ten times the specified maximum carbon monoxide content.

d) Use a gas chromatograph such as that described in 6.7 a). The technique utilized shall be specific for the separation and analysis of carbon monoxide.

e) Use a catalytic methanator gas chromatograph such as that described in 6.7 a).

#### 6.10 Mercury vapour content

The mercury vapour content shall be determined using one of the following procedures.

- a) Use a gas-cell-equipped absorption-type ultraviolet analyser, calibrated at appropriate intervals with mercury vapour standards or integrally with a mechanical calibrating device. The range used shall be no greater than ten times the specified maximum mercury vapour content.
- b) Use a titrimetric analytical technique in which mercury reacts to form a compound whose content is subsequently measured.
- c) Use a thin gold film sensor-based analyser used in conjunction with a gold coil collection device.

#### 6.11 Total sulfur content

The determination of the content of inorganic and organic sulfur compounds shall be carried out using one of the following procedures.

- a) Use an oxy-hydrogen flame-type combustion method. An oxy-hydrogen flame, whose sulfur contents have been removed completely by absorption or other suitable method, shall be used to burn the sample at a high temperature. The combustion products are absorbed in hydrogen peroxide/water to oxidize the sulfur to sulfuric acid, after which the sulfur content is determined and calculated as sulfur dioxide.
- b) Use a flame-photometer-type detector for gas chromatograph, without a separating tube, which measures the flame absorbance emitted [see 6.7 a)].

#### 6.12 Permanent particulates

This International Standard recognizes that it is not possible to assure any specific amount of permanent particulates in gaseous hydrogen and no limits are specified. In-line filtration requirements for transfer of hydrogen product should be established between the supplier and the customer.

In order to reduce the amount of permanent particulates in liquid hydrogen, the liquid may be filtered during transfer. The equipment commonly used is a 10  $\mu$ m to 40  $\mu$ m (10  $\mu$ m nominal, 40  $\mu$ m absolute) filter assembly installed in the transfer system.

#### 7 Safety and detection

## 7.1 Safety

Hydrogen is flammable and can be an asphyxiant. The sampling and testing of hydrogen involve very hazardous procedures. Users of hydrogen shall be familiar with the physical, chemical and specific hazardous properties of gaseous hydrogen (GH<sub>2</sub>), liquid hydrogen (LH<sub>2</sub>) and slush hydrogen (SLH<sub>2</sub>) where applicable.

## 7.2 Detection

The use of a colorant or an odorant in the hydrogen product has been proposed as a means of flame and gas detection. In those cases where it is difficult to provide this feature in the product itself, it is recommended that system designers incorporate appropriate detection and monitoring systems if odorants are not used. The introduction of impurities in hydrogen for purposes of detection may not be compatible with such concepts as hydrogen storage in hydride or fuel cells. To date an odorant has not been identified which will dissolve in liquid hydrogen and which may be used in the hydrogen fuel supply chain.

# **Bibliography**

[1] ASTM D 1946:1990, Standard Practice for Analysis of Reformed Gas by Gas Chromatography.



**Descriptors:** fuels, gaseous fuels, liquefied gases, hydrogen, classification, specifications, characteristics, determination of content, impurities.

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