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Hydrogen fuel — Product specification —

Part 3:

Proton exchange membrane (PEM) fuel cell applications for stationary appliances

Carburant hydrogène - Spécification de produit —

Partie 3: Applications des piles à combustible à membrane à échange de protons (PEM) pour appareils stationnaires

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 197, *Hydrogen technologies.*

ISO 14687 consists of the following parts, under the general title *Hydrogen fuel— Product specification*:

— *Part 1: All applications except proton exchange membrane (PEM) fuel cell for road vehicles*

— *Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles*

— *Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances*

Introduction

This part of ISO 14687 provides an initial, albeit incomplete, basis for describing a common fuel to be used by proton exchange membrane (PEM) fuel cell applications for stationary appliances in the near term.

A large number of fuel cells are presently commercialized as power sources for stationary applications, such as distributed, supplementary, and back-up power generation and as stationary heat and power cogeneration systems. Most stationary fuel cells are equipped with a fuel processing system which converts fossil fuel to hydrogen-rich fuel composed primarily of hydrogen and carbon dioxide. Some of the stationary fuel cells use hydrogen fuel of high purity supplied through high pressure tanks or pipeline from a distant hydrogen production plant.

The purpose of this part of ISO 14687 is to establish an international standard of quality characteristics of hydrogen fuel for stationary fuel cells.

Types of fuel cells other than proton exchange membrane fuel cells (PEMFC), such as phosphoric acid fuel cell (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC), may require similar standards in future. Thus, it is anticipated that in the future PAFC, MCFC and SOFC hydrogen fuel quality requirements will be added as amendments to this part of ISO 14687.

This part of ISO 14687 is intended to consolidate the hydrogen fuel product specification needs anticipated by PEM fuel cell manufacturers and hydrogen fuel suppliers as both industries proceed toward achieving wide-spread commercialization. Monitoring hydrogen fuel quality is necessary because specific impurities will adversely affect the fuel cell power system. In addition, there may be performance implications in the fuel cell power system if certain non-hydrogen constituent levels are not controlled. Methods to monitor the hydrogen fuel quality that is delivered to these stationary appliances are addressed.

This part of ISO 14687 specifies one grade of hydrogen, Type I, grade E, with three categories for different target applications. Quality verification should be determined at the inlet point of a PEM fuel cell power system.

Since PEM fuel cell applications for stationary appliances and related technologies are developing rapidly, this part of ISO 14687 will be revised according to technological progress as necessary. Additionally, some of the impurity limits are dictated by current analytical capabilities, which are also in the process of development. Technical Committee ISO/TC 197, *Hydrogen technologies*, will monitor this technology trend. It is also noted that this part of ISO 14687 has been prepared to assist in the development of PEM fuel cell applications for stationary appliances and related technologies.

Further research and development efforts should focus on, but not be limited to:

- PEM fuel cell catalyst and fuel cell tolerance to hydrogen fuel impurities;
- Effects/mechanisms of impurities on fuel cell power systems and components;
- Impurity detection and measurement techniques for laboratory, production, and in-field operations; and,
- Stationary fuel cell demonstration results.

Hydrogen fuel — Product specification —

Part 3:
Proton exchange membrane (PEM) fuel cell applications for stationary appliances

1 Scope

This part of ISO 14687 specifies the quality characteristics of hydrogen fuel in order to ensure uniformity of the hydrogen product for utilization in stationary proton exchange membrane (PEM) fuel cell power systems.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6145 (all parts), *Gas analysis — Preparation of calibration gas mixtures using dynamic methods*

ISO 14687-1, *Hydrogen fuel — Product specification — Part 1: All applications except proton exchange membrane (PEM) fuel cell for road vehicles*

ISO 14687-2, *Hydrogen fuel — Product specification — Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles*

IEC/TS 62282-1, *Fuel cell technologies — Terminology*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14687-1, IEC/TS 62282-1 and the following apply.

3.1
boundary point
point between the hydrogen fuel supply equipment and the PEM fuel cell power system at which the quality characteristics of the hydrogen fuel are to be determined

3.2
constituent
component (or compound) found within a hydrogen fuel mixture

3.3
contaminant
impurity that adversely affects the component parts within the fuel cell power system or the hydrogen storage system

Note 1 to entry: An adverse effect can be reversible or irreversible.

3.4
customer
party responsible for sourcing hydrogen fuel in order to operate the fuel cell power system

3.5
detection limit
lowest quantity of a substance that can be distinguished from the absence of that substance with a stated confidence limit

3.6
determination limit
lowest quantity which can be measured at a given acceptable level of uncertainty

3.7
fuel cell
electrochemical device that converts the chemical energy of a fuel and an oxidant to electrical energy (DC power), heat and other reaction products

3.8
hydrogen fuel
gas containing a concentration of hydrogen equal to or larger than 50 % used for stationary fuel cell applications

3.9
hydrogen fuel index
fraction or percentage of a fuel mixture that is hydrogen

3.10
hydrogen fuel supply equipment
equipment used for the transportation or on-site generation of hydrogen fuel, and subsequently for delivery to the fuel cell power system, including additional storage, vaporization, and pressure regulation as appropriate

3.11
irreversible effect
effect, which results in a permanent degradation of the fuel cell power system performance that cannot be restored by practical changes of operational conditions and/or gas composition

3.12
particulate
solid or aerosol particle, including oil mist, that may be entrained in the hydrogen entering a fuel cell

3.13
reversible effect
effect, which results in a temporary degradation of the fuel cell power system performance that can be restored by practical changes of operational conditions and/or gas composition

3.14
stationary proton exchange membrane (PEM) fuel cell power system
self-contained assembly of integrated PEM fuel cell systems used for the generation of electricity which is fixed in place in a specific location, typically containing the following subsystems: fuel cell stack, air processing, thermal management, water management, and automatic control system and which is used in applications such as: distributed power generation, back-up power generation, remote power generation, electricity and heat co-generation for resident and commercial applications

Note 1 to entry: For the purposes of this part of ISO 14687, the PEM fuel cell power system does not contain a fuel processing system due to the location of the boundary point.

3.15
system integrator
integrator of equipment between the PEM fuel cell power system and the hydrogen supply

4 General design requirements

4.1 Classification

Hydrogen fuel for PEM fuel cell applications for stationary appliances shall be classified as Type I, grade E, gaseous hydrogen fuel for PEM fuel cell stationary appliance systems.

NOTE 1 Type I, grade A, B, C, Type II, grade C and Type III, which are applicable for all applications except PEM fuel cells for road vehicles and stationary appliances, are defined in ISO 14687-1.

NOTE 2 Type I, grade D and Type II, grade D, which are applicable for PEM fuel cells for road vehicles are defined in ISO 14687-2.

4.2 Categories

Type I, grade E hydrogen fuel for PEM fuel cell applications for stationary appliances specifies the following subcategories for the convenience of both PEM fuel cell manufacturers and hydrogen fuel suppliers:

- Type I, grade E, Category 1
- Type I, grade E, Category 2
- Type I, grade E, Category 3

These categories are defined to meet the needs of different stationary applications, depending on the requirements specified by the manufacturer.

4.3 Limiting characteristics

The fuel quality at the boundary point set between the hydrogen fuel supply equipment and the PEM fuel cell power system, as applicable to the aforementioned grades of hydrogen fuel for stationary appliance systems, shall meet the requirements of Table 1.

NOTE 1 Please see Annex A for the selection of the boundary point.

NOTE 2 Annex B provides the rationale for the selection of the impurities specified in Table 1.

Table 1 — Directory of limiting characteristics

Characteristics[a] (assay)	Type I, grade E		
	Category 1	**Category 2**	**Category 3**
Hydrogen fuel index (minimum mole fraction)	50 %	50 %	99,9 %
Total non-hydrogen gases (maximum mole fraction)	50 %	50 %	0,1 %
Water (H_2O)[b]	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions
Maximum concentration of individual contaminants			
Total hydrocarbons (C_1 basis)[c]	10 µmol/mol	2 µmol/mol	2 µmol/mol
Oxygen (O_2)	200 µmol/mol	200 µmol/mol	50 µmol/mol
Nitrogen (N_2), Argon (Ar), Helium (He) (mole fraction)	50 %	50 %	0,1 %
Carbon dioxide (CO_2)	Included in total non-hydrogen gases	Included in total non-hydrogen gases	2 µmol/mol
Carbon monoxide (CO)	10 µmol/mol	10 µmol/mol	0,2 µmol/mol
Total sulfur compounds[d]	0,004 µmol/mol	0,004 µmol/mol	0,004 µmol/mol
Formaldehyde (HCHO)	3,0 µmol/mol	0,01 µmol/mol	0,01 µmol/mol
Formic acid (HCOOH)	10 µmol/mol	0,2 µmol/mol	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol	0,1 µmol/mol	0,1 µmol/mol
Total halogenated compounds[e]	0,05 µmol/mol	0,05 µmol/mol	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg	1 mg/kg	1 mg/kg
Maximum particle diameter	75 µm	75 µm	75 µm

NOTE For the constituents that are additive (i.e. total hydrocarbons, total sulfur compounds and total halogenated compounds), the sum of the constituents shall be less than or equal to the specifications in the table. It is therefore important that the analytical method used measures the *total* concentration of these families of compounds, and not the concentration of single compounds within these families, which are subsequently summed to give a total amount of fraction. The latter approach risks a false negative being reported. For more details, see Clause 7.

[a] Maximum concentration of impurities against the total gas content shall be determined on a dry-basis.

[b] Each site shall be evaluated to determine the appropriate maximum water content based on the lowest expected ambient temperature and the highest expected storage pressure.

[c] Total hydrocarbons are measured on a carbon basis (µmolC/mol). The specification for total hydrocarbons includes oxygenated hydrocarbons. The measured amount fractions of all oxygenated hydrocarbons shall therefore contribute to the measured amount fraction of total hydrocarbons. Specifications for some individual oxygenated hydrocarbons (e.g. formaldehyde and formic acid) are also given in the table. These, however, also contribute to the measured amount fraction of total hydrocarbons. These species have been assigned their own specifications based on their potential to impair the performance of PEM fuel cells. Total hydrocarbons may exceed the limit due only to the presence of methane, in which case the methane shall not exceed 5 % for Category 1, 1 % for Category 2 or 100 µmol/mol of hydrogen fuel for Category 3.

d As a minimum, total sulfur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

e Includes, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl_2), and organic halides (R-X).

4.4 Hydrogen production guidance

Hydrogen fuel may be produced in a number of ways, including reformation of natural gas or other fossil or renewable fuels, the electrolysis of water and numerous biological methods. Hydrogen fuel can be generated on-site, generally in relatively small quantities, or in a larger scale production system off-site, then transported under pressure or as a liquid to the point of use.

NOTE Biological sources of hydrogen can contain additional species that affect fuel cell performance (e.g. siloxanes and mercury). Such species are not included in Table 1 due to insufficient data.

5 Quality verification

5.1 General requirements

Quality verification requirements shall be determined at the boundary point using the sampling and analytical methods specified in Clauses 6 and 7 respectively. Alternatively, the quality verification may be performed at other locations or under other methods by written agreement between the supplier and the customer.

Analysis of all limiting characteristics in Table 1 may not be necessary for all hydrogen production methods, if acceptable to the customer.

All analyses conducted in this part of ISO 14687 shall be undertaken using gaseous calibration standards (or other calibration devices) that are traceable to the International System of Units (SI) via national standards, where such standards are available.

5.2 Analytical requirements of the qualification tests

The frequency of testing and analytical requirements for the qualification tests shall be specified by the supplier and the customer. Consideration shall be given to the consistency of hydrogen supply in determining test frequency and constituents to be tested.

NOTE Annex C provides a recommended practice of the quality assurance for steam methane reforming (SMR) hydrogen production processes using pressure swing adsorption (PSA) purification.

5.3 Report results

The detection and determination limits for analytical methods and instruments used shall be reported along with the results of each test and the date the sample was taken.

6 Sampling

6.1 Sample size

Where possible, the quantity of hydrogen in a single sample container should 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. A large sample or sample with a greater pressure, where applicable, may be required if multiple tests are to be conducted.

6.2 Selection of the sampling point

A boundary point shall be established so that gaseous samples are representative of the hydrogen supplies to the PEM fuel cell power systems.

NOTE Annex A provides guidance to assist in the identification of the party responsible for the quality of hydrogen at the boundary point and also the selection of the boundary point.

6.3 Sampling procedure

Gaseous hydrogen samples shall be representative of the hydrogen supply, and withdrawn from the boundary point through a suitable connection into an appropriately sized sample container. No contamination of the hydrogen fuel shall be introduced between the boundary point and the sample container (a suitable purge valve may be used).

Attention shall be paid to ensure that the sampled hydrogen is not contaminated with residual gases inside the sample container by evacuating it. If evacuation is not possible, the sample container shall be cleaned using repeated purge cycles.

Sampled gases are flammable and potentially toxic. Measures shall be taken to avoid hazardous situations as per Clause 9.

6.4 Particulates in gaseous hydrogen

Particulates in hydrogen shall be sampled from the boundary point, using a filter, if practical, under the same conditions (pressure and flow rate) as employed in the actual hydrogen supplying condition. Appropriate measures shall be taken for the sample gas not to be contaminated by particulates coming from the connection device and/or the ambient air.

7 Analytical methods

7.1 General

The analytical methods specified in Clause 7 shall be used for measuring characteristics listed in Table 1. Annex D provides a list of standard analytical techniques.

7.2 Parameters of analysis

The determination limits as defined in Clause 8 for the analytical methods listed should be less than or equal to the limiting characteristics of hydrogen for all impurities listed in Table 1. Detection limits shall be at least three times lower than the specifications listed in Table 1.

Calibration gas standards that contain the applicable gaseous components at applicable concentrations and standardized dilution procedures shall be used to calibrate the analytical instruments used to determine the limiting characteristics of hydrogen. The calibration gas mixture shall be prepared in accordance with ISO 6142 or ISO 6145.

The calibration of measuring equipment shall be traceable to a primary standard if possible.

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

7.3 Water content

The water content shall be determined using one of the following instruments:

a) An electrostatic capacity type moisture meter;

b) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength, and detector;

c) A gas chromatograph with a mass spectrometer (GC-MS) with or without jet pulse injection;

d) A vibrating quartz analyser;

e) A cavity ring down spectroscopy (CRDS);

f) An electrolytic cell analyser; or,

g) Other validated analytical methods capable of meeting the specifications in Table 1.

Alternatively, water content may be determined with a dew point analyser in which the temperature of a viewed surface is measured at the time moisture first begins to form.

7.4 Total hydrocarbon content

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

a) A gas chromatograph with a flame ionization detector (GC/FID);

b) A flame ionization detector (FID) based total hydrocarbon analyser;

c) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector;

d) A gas chromatograph with a mass spectrometer (GC-MS) with a concentrating device; or,

e) Other validated analytical methods capable of meeting the specifications in Table 1.

7.5 Oxygen content

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

a) A galvanic cell type oxygen analyser;

b) A gas chromatograph with a mass spectrometer (GC-MS) with jet pulse injection;

c) A gas chromatograph with thermal conductivity detector (GC/TCD);

d) A gas chromatograph with pulsed discharge helium ionization detector (GC/PDHID);

e) An electrochemical sensor; or,

f) Other validated analytical methods capable of meeting the specifications in Table 1.

7.6 Helium content

The helium content in hydrogen can be determined using a gas chromatograph with thermal conductivity detector (GC/TCD) or a gas chromatograph with a mass spectrometer (GC-MS).

7.7 Argon and nitrogen contents

The argon and nitrogen contents shall be determined using one of the following instruments:

a) A gas chromatograph with thermal conductivity detector (GC/TCD);

b) A gas chromatograph with pulsed discharge helium ionization detector (GC/PDHID);

c) A gas chromatograph with a mass spectrometer (GC-MS) with jet pulse injection; or,

d) Other validated analytical methods capable of meeting the specifications in Table 1.

7.8 Carbon dioxide content

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

a) A gas chromatograph with a catalytic methanizer and a flame ionization detector (GC/CM&FID);

b) A gas chromatograph with pulsed discharge helium ionization detector (GC/PDHID);

c) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector;

d) A gas chromatograph with a mass spectrometer (GC-MS) with jet pulse injection; or,

e) Other validated analytical methods capable of meeting the specifications in Table 1.

7.9 Carbon monoxide content

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

a) A gas chromatograph with a catalytic methanizer and a flame ionization detector (GC/CM&FID);

b) A gas chromatograph with pulsed discharge helium ionization detector (GC/PDHID);

c) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector; or,

d) Other validated analytical methods capable of meeting the specifications in Table 1.

7.10 Total sulfur content

The content of inorganic and organic sulfur compounds shall be determined using a gas chromatograph with a sulfur chemiluminescence detector (GC/SCD) with or without concentration device.

Alternatively, an oxy-hydrogen flame, of which any sulfur content has been removed completely by absorption or by another suitable method, may be used to burn the sample at a high temperature. If this technique is used, the combustion products shall be absorbed in hydrogen peroxide/water to oxidize the sulfur to sulphuric acid, after which the content shall be determined and calculated as sulfur dioxide. The sulfur content analysis shall then be conducted with an ion chromatography technique, capable of separating and detecting the desired component. Appropriate impurity-concentrating techniques may be used to attain the sensitivity.

The analytical method used to measure total sulfur compounds shall measure the *total* amount fraction of sulfur compounds

7.11 Formaldehyde content

The formaldehyde content shall be determined using one of the following instruments:

a) A gas chromatograph with a flame ionization detector (GC/FID);

b) A gas chromatograph with pulsed discharge helium ionization detector (GC/PDHID);

c) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector;

d) A gas chromatograph with a mass spectrometer (GC-MS) with a concentration device; or,

e) Other validated analytical methods capable of meeting the specifications in Table 1.

Alternatively, the formaldehyde may be absorbed in a 2,4-dinitrophenylhydrazine cartridge by passing the sampled hydrogen through the cartridge and then extracting it from the cartridge with solvent. If this technique is used, the extraction liquid shall be analysed with a high-performance liquid chromatography technique, capable of separating and detecting the desired component. Appropriate impurity-concentrating techniques may be used to attain the sensitivity.

7.12 Formic acid content

The formic acid content shall be determined using one of the following instruments:

a) A Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector;

b) A gas chromatograph with a mass spectrometer (GC-MS) with a concentration device; or,

c) Other validated analytical methods capable of meeting the specifications in Table 1.

Alternatively, the hydrogen fuel may be passed through an appropriate absorbing solution (e.g. sodium carbonate) and analysed for formate ion (HCOO) content using an ion chromatograph (IC).

7.13 Ammonia content

The ammonia content shall be determined using a Fourier Transform Infrared spectrometer (FTIR) with suitable cell path length, scan wavelength and detector. Alternatively, the hydrogen fuel may be passed through an appropriate absorbing solution and analysed for ammonium ion (NH_4^+) content with an ion chromatograph (IC).

7.14 Total halogenated compounds

The analytical method used to measure halogenated compounds should ideally measure the *total* amount fraction of halogenated compounds.

Halogenated compounds shall be determined using one of the following instruments:

a) A gas chromatograph with electron capture detection (GC/ECD), with concentration device for HBr, HCl, and Cl_2;

b) A gas chromatograph with a mass spectrometer (GC-MS) with a concentration device for organic halides; or,

c) Other validated analytical methods capable of meeting the specifications in Table 1.

Alternatively, the hydrogen fuel may be passed through an appropriate absorbing solution and analysed for fluoride ion (F^-), chloride ion (CI^-) and bromide ion (Br^-) content using an ion chromatograph (IC). If this technique is used, the choice of absorbing solution shall depend on the components expected in the sample. As an example, if the halogenated compounds are expected to be F_2, CI_2, Br_2, HF, HCI and HBr, a sodium hydroxide solution may be used, but this will not be suitable for an organic halogenated compound.

7.15 Particulates concentration

The particulates concentration shall be determined by using the following procedure. The particles sampled with the filter such as that described in 6.4 shall be weighed. The particulates concentration shall be calculated from the mass of hydrogen flow through the filter.

7.16 Particulate size

The particulate size shall be determined by using the following procedure. The particles sampled with a filter such as that described in 6.4 shall be observed using a low power stereobinocular microscope, a polarizing light microscope, a scanning electron microscope or another type of appropriate microscope. The microscope shall be able to observe particles equal to or less than 75 µm, and no particulates of 75 µm or more in diameter shall be found. If a filter with the diameter of 75 µm is used, no particulates shall be found left on the filter.

8 Detection limit and determination limit

Generally, detection limit and determination (quantification) limit are based on the ratio of the signal to the noise of analytical instruments and on standard deviation (sigma) of the data. The effects of concentrating techniques shall be considered. In cases where analysis results are less than the detection limit, they shall be reported as “below detection limit”.

To establish detection and determination limits, the detection and determination limit provided by the hardware specification of analytical equipment shall be referred to and confirmed.

In cases where no detection and determination numbers are provided by the hardware specification of analytical equipment, 3 sigma and 10 sigma shall be employed for the detection and determination limits, respectively.

NOTE Annex D provides the detection and determination limits for the analytical methods described in Clause 7.

9 Safety

Hydrogen is flammable and can be an asphyxiant. The sampling and testing of hydrogen may be hazardous. Users of hydrogen shall be familiar with its physical and chemical properties as well as specific hazards associated with the use of hydrogen as applicable, and shall develop appropriate risk management measures.

Additionally, the hydrogen fuel may contain constituents that are toxic. Precautions shall be taken to avoid exposure, where appropriate.

Guidance for the safe use of hydrogen in its gaseous and liquid forms can be found in ISO/TR 15916.

Annex A
(informative)

Guidance on the selection of the boundary point

A.1 Purpose

The following guidance is provided to assist in the identification of the boundary point and of the party responsible for the quality of hydrogen at the boundary point.

A.2 Identification of the party responsible for hydrogen quality at the sampling point

It is recognized that provision of hydrogen to a fuel cell power system may involve numerous parties.

The following text and figure provide examples for information purposes, but are not intended to be comprehensive. Hydrogen delivery systems that incorporate different equipment or hydrogen feedstock should use these examples as a basis for determining responsibility for the quality of hydrogen at the boundary point and if appropriate, additional sampling points.

The following are examples of parties involved in and responsible for the supply of hydrogen:

- Gaseous hydrogen supplier (cylinders or tube trailers);
- Liquid hydrogen supplier;
- Hydrogen via pipeline distributer;
- Reformer manufacturer;
- Electrolyser manufacturer.

Depending on the form of the hydrogen supply, there may be a requirement for system integrators to provide equipment between the source of the hydrogen and the inlet to the fuel cell power system. Such equipment may comprise, as applicable, the following, as shown in Figure A.1:

- Pressure regulators;
- Liquid hydrogen storage, cryogenics pumps and vaporizers;
- Gaseous hydrogen buffer storage;
- Additional manifolds from hydrogen source to fuel cell power system inlet.

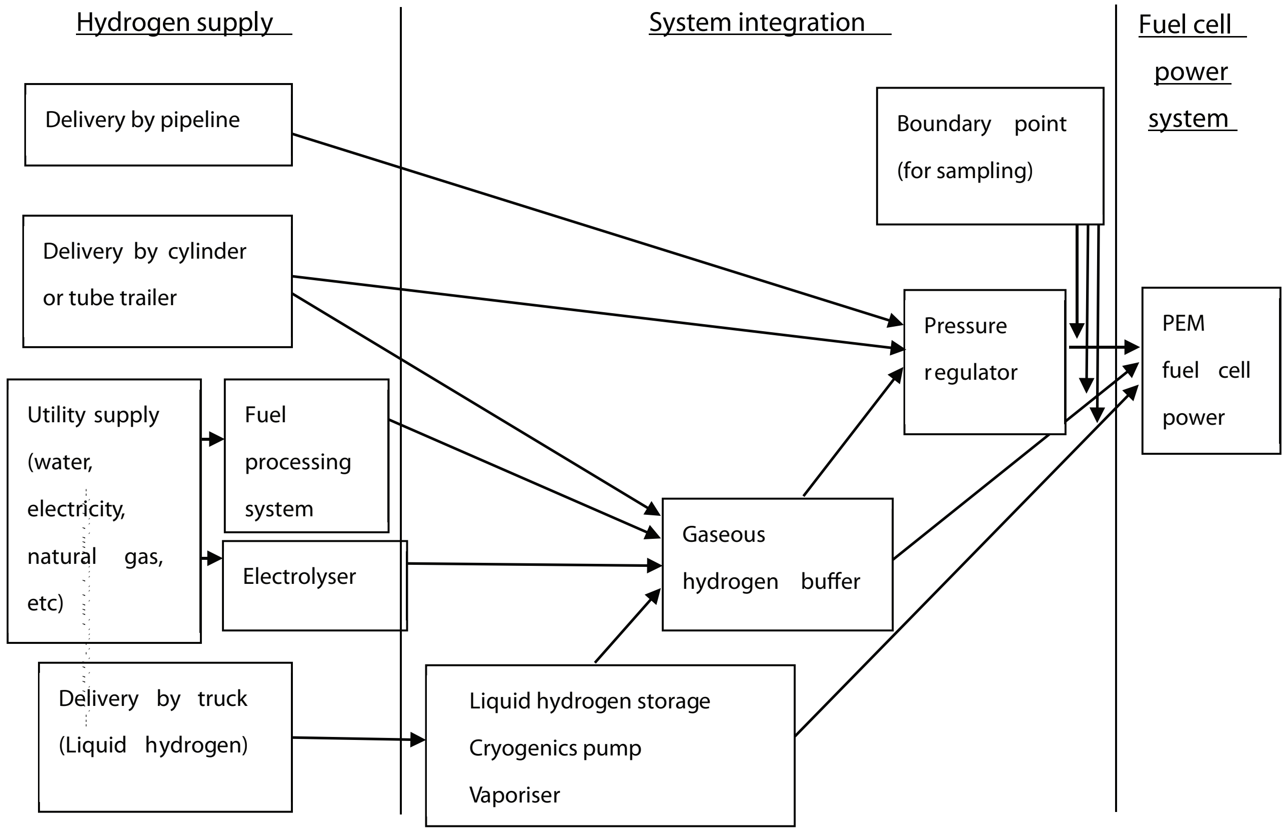


Figure A.1 — Examples showing the supply of hydrogen to a fuel cell power system and position of the boundary point

It should be recognized that the system integrator is responsible for the quality of hydrogen at the boundary point, immediately prior to the inlet of the fuel cell power system. If the system integrator and fuel cell power system operator are the same party, one or more appropriate alternative sampling points for meeting hydrogen quality characteristics should be determined by agreement between the hydrogen supplier and the customer.

In some cases, the system integrator may also be the hydrogen supplier, in which case the responsibility for the hydrogen quality characteristics at the boundary point is that of the hydrogen supplier unless otherwise specified by agreement between the hydrogen supplier and the customer.

Where the system integrator and hydrogen supplier are different parties, the responsibility for the hydrogen quality characteristics at the boundary point is that of the system integrator. In such cases, the analytical requirements (periodicity, impurities, and appropriate interface test point) for the hydrogen supply should be determined by agreement between the hydrogen supplier, the system integrator and the customer.

It may also be the case that the hydrogen supplier provides some aspects of on-site system integration but does not directly interface with the fuel cell power system. In such cases, the hydrogen supplier is responsible for meeting the hydrogen quality characteristics at the supplier interface to the additional equipment that connects to the fuel cell power system, while the integrator interfacing with the fuel cell power system is responsible for the analytical requirements of the hydrogen quality at the boundary point. The analytical requirements (periodicity, impurities) at any additional sampling points appropriate to the system should be specified by agreement between the system integrator and the hydrogen supplier.

Where system maintenance is to be carried out by an additional party, the requirements for hydrogen quality assurance following completion of such maintenance should be determined by agreement between the system integrator, the party responsible for maintenance and the fuel cell operator.

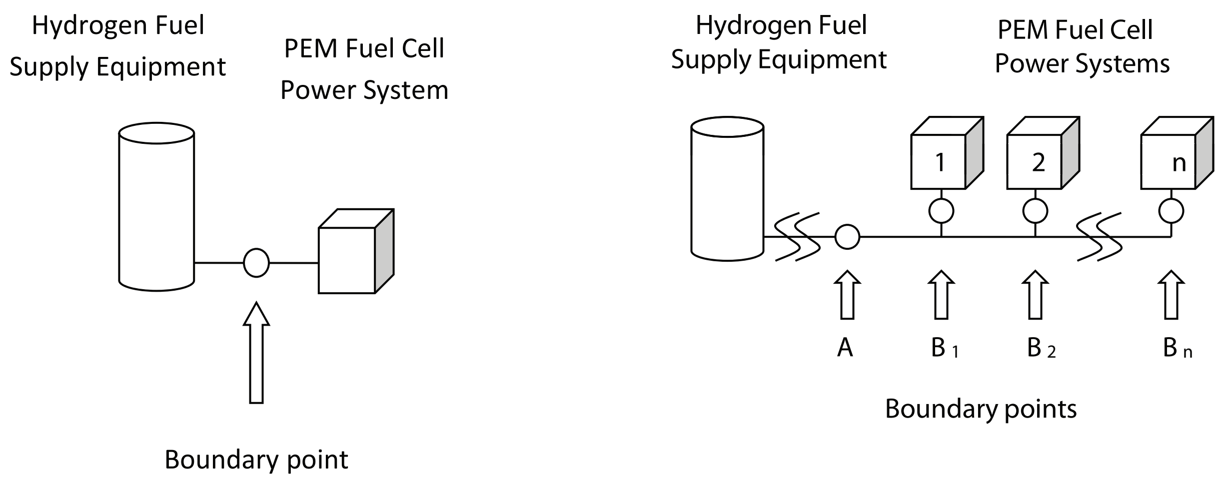
A.3 Selection of the sampling point

In the case of a single fuel cell power system, as shown in Figure A.2 a), the boundary point should be as close as practical to the fuel inlet to the fuel cell power system.

In the case of multiple fuel cell power systems in parallel, as shown in Figure A.2 b), the location of the boundary point should be determined by agreement between the system integrator and the fuel cell operator, subject to national and local regulations.

Examples for the location of the sampling point may include:

- Boundary point A - the supply for fuel cell power systems 1 to n.
- A single boundary point between B_1 and B_n, representing the worst case.
- All boundary points B_1 through B_n.



a) Single fuel cell power system

b) Multiple fuel cell power systems in parallel

Figure A.2 — Positioning of sampling point

Annex B
(informative)

Rationale for the selection of hydrogen impurities to be measured

B.1 Water content

Water (H_2O) generally does not affect the function of a fuel cell, however, it provides a transport mechanism for water-soluble contaminants such as K^+ and Na^+ when present as an aerosol. Both K^+ and Na^+ are recommended not to exceed 0,05 µmol/mol for Category 3. In addition, water may pose a concern under sub-zero ambient conditions and affect valves. Thus, water shall remain gaseous throughout the encountered ambient temperature conditions.

B.2 Total hydrocarbon content

Different hydrocarbons have different effects on fuel cell performance. Generally, aromatic hydrocarbons adsorb more strongly on the catalyst surface than alkanes, inhibiting access to hydrogen. Methane (CH_4) is considered an inert gas since its effect on fuel cell performance is to dilute the hydrogen fuel stream.

B.3 Oxygen content

Oxygen (O_2) in low concentrations does not adversely affect the function of the fuel cell power system, but high concentration oxygen causes degradation of the fuel cell.

B.4 Helium, nitrogen and argon contents

Inert constituents, such as helium (He), nitrogen (N_2) and argon (Ar) do not adversely affect the function of fuel cell components or a fuel cell power system. However, they dilute the hydrogen gas.

B.5 Carbon dioxide content

Carbon dioxide (CO_2) does not typically affect the function of fuel cells. It dilutes the hydrogen fuel thereby affecting the efficiency of the fuel cell power system. A high CO_2 content in hydrogen fuel (>1000ppm) will result in the formation of CO via a reverse water gas shift reaction which, depending on the material selection and/or system design and operation, could further impact fuel cell performance.

B.6 Carbon monoxide content

Carbon monoxide (CO) is a severe catalyst poison that adversely affects fuel cell performance and thus needs to be kept at very low levels in hydrogen fuel. While the impact on performance can be reversed by changing operating conditions and/or gas composition, these measures may not be practical. In reformate applications (Categories 1 and 2) the impact of the inherently higher CO levels is mitigated through material selection, and/or system design and operation. Nonetheless the long term effect of CO on fuel cell durability is a concern, specifically for low anode catalyst loadings.

B.7 Total sulfur concentration

Sulfur containing compounds are catalyst poisons that at even very low levels can cause some irreversible degradation of fuel cell performance. The minimum specific sulfur compounds that need to be included in the testing are: hydrogen sulphide (H_2S), carbonyl sulphide (COS), carbon disulphide (CS_2), and mercaptans (e.g. methyl mercaptan), which may be found in hydrogen reformed from natural gas. It is recommended that total sulfur concentration be monitored. Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants.

B.8 Formaldehyde and formic acid contents

Formaldehyde (HCHO) and formic acid (HCOOH) have a similar effect on fuel cell performance as CO and are thus considered as reversible contaminants. The effect of HCHO and HCOOH on fuel cell performance can be more severe than that of CO due to slower recovery kinetics and their specifications are lower than that for CO. Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants.

B.9 Ammonia content

Ammonia (NH_3) causes some irreversible fuel cell performance degradation by contaminating the proton exchange membrane/ionomer and reacting with protons in the membrane/ionomer to form NH_4^+ ions. Test data for ammonia tolerance should include ion exchange capacities of membrane and/or electrodes. Lower catalyst loadings imply lower ion exchange capacities within the electrode.

B.10 Total halogenated compounds contents

Halogenated compounds cause irreversible performance degradation. Potential sources include chlor-alkali production processes, refrigerants used in processing, and cleaning agents.

B.11 Particulates

A maximum particulate concentration and size are specified to ensure that filters are not clogged and/or particulates do not enter the PEM fuel power system and affect the operation of valves and fuel cell stacks. Potassium and sodium ions present in aerosols cause irreversible performance degradation by contaminating the proton exchange membrane/ionomer. Iron-containing particulates, even at very low concentrations, cause severe membrane/ionomer degradation.

Annex C
(informative)

Pressure swing adsorption and applicability of CO as canary species

C.1 Canary species: major impurities from different H2 production and purification processes

For SMR-PSA production and purification, CO can serve as a canary species for the presence of other impurities listed in Table 1. Canary species can serve as an indicator of the presence of other chemical constituents because it has the highest probability of presence in a fuel produced by a given process. Confirmation that CO content is less than its specified limit indicates that other impurities, except inerts, are present at less than their specified limits.

The maximum content of inerts in the product hydrogen can be estimated by using the maximum content of inerts in the feedstock specified by the supplier and the flow increase in the SMR system and the flow decrease in the PSA system. The flow increase in the SMR system and the flow decrease in the PSA system can be calculated from the feedstock composition, steam to carbon ratio, and hydrogen conversion rate.

C.2 In-line monitoring of the canary species

In-line monitoring of CO is strongly recommended to show that its content in the hydrogen fuel is less than the specification on real-time basis, which indicates that other contaminants are less than their specifications on real-time basis. For this purpose, commercially available infrared CO analyzers can be used. In the case of a SMR-PSA system, the analyser should be placed just after the SMR-PSA system to avoid contamination of the equipment downstream.

C.3 Batch analysis

For back-up of in-line monitoring of CO content, batch sampling of product hydrogen and laboratory analyses of all impurities species as listed in Table 1 are also recommended. The batch sample should be taken at the boundary point. The frequency of sampling and analysis is determined by the hydrogen supplier. The analytical methods as described in Clauses 6 and 7 should be applied.

Annex D
(informative)

Detection and determination limits of the analytical methods for determination of the limiting characteristics of hydrogen

D.1 General

This Annex, as informative, is intended to provide a list of detection and determination limits of the analytical methods to verify compliance with the specifications listed in Table 1. Table D.1 provides a list of detection and determination limits of the analytical methods listed in this part of ISO 14687. The information in this table is likely to change as analysis technologies and equipment continues to develop.

Table D.1 — Suggested analytical methods with detection and determination limits

Impurities	Analytical methods	Detection limit µmol/mol (unless otherwise noted)	Determination limit µmol/mol (unless otherwise noted)	Example of test methods that could be used
Water (H_2O)	Dew point analyser	0,5	1,7	JIS K0225
	GC-MS with jet pulse injection	1	3	ASTM D7649–10 JIS K0123
	GC-MS with direct injection	0,8	2,4	NPL Report AS 64
	Vibrating quartz analyser	0,02	0,07	JIS K0225
	Electrostatic capacity type moisture meter	0,04	0,1	JIS K0225
	FTIR	0,12 1	0,4 3	ASTM D7653–10 JIS K0117
	Cavity ring-down spectroscopy	0,01	0,03	NPL Report AS 64
Total hydrocarbons (C1 basis)	FID	0,1	0,3	ASTM D7675–11
	GC/FID	0,01 – 0,1	0,03 – 1,0	JIS K0114
	FTIR	0,01	0,03	JIS K0117
Oxygen (O_2)	Galvanic cell O_2 meter	0,01	0,03	JIS K0225
	GC-MS with jet pulse injection	1	3	ASTM D7649–10
	GC/PDHID	0,006	0,018	NPL Report AS 64
	GC/TCD	3	9	NPL Report AS 64
	Electrochemical Sensor	0,1	0,3	ASTM D7607–11
Helium (He)	GC/TCD	3 – 5	10 – 15	ASTM D1945–03 JIS K0114
	GC-MS	10	30	JIS K0123

Table D.1 *(continued)*

Impurities	Analytical methods	Detection limit µmol/mol (unless otherwise noted)	Determination limit µmol/mol (unless otherwise noted)	Example of test methods that could be used
Nitrogen (N_2), Argon (Ar)	GC-MS with jet pulse injection	5 (N_2), 1 (Ar) 0,03	15 (N_2), 3 (Ar) 0,1	ASTM D7649–10 JIS K0123
	GC/TCD	1 – 3	3 – 10	JIS K0114
	GC/PDHID	0,001	0,01	JIS K0114
Carbon dioxide (CO_2)	GC-MS with jet pulse injection	0,5 0,01	1,5 0,03	ASTM D7649–10 JIS K0123
	GC/FID with methanizer	0,01	0,03	JIS K0114
	GC/PDHID	0,001	0,01	JIS K0114
	FTIR	0,01 0,02	0,03 0,06	ASTM D7653–10 JIS K0117
Carbon monoxide (CO)	GC/FID with methanizer	0,01	0,03	JIS K0114
	FTIR	0,01 0,1	0,03 0,3	ASTM D7653–10 JIS K0117
	GC/PDHID	0,001	0,01	JIS K0114
Total sulfur compounds	IC with concentrator	0,0001 – 0,001	0,0003 – 0,004	JIS K0127
	GC/SCD (Sulfur Chemiluminescence Detector) with concentrator	0.00002 0,001	0.00006 0,003	ASTM D7652–11 JIS K0114
	GC/SCD without pre-concentration	0,001	0,003	NPL Report AS 64
Formaldehyde (HCHO)	DNPH/HPLC	0,002 – 0,01	0,006 – 0,03	JIS K0124
	GC/PDHID	0,01	0,03	JIS K0114
	FTIR	0,02 0,01	0,06 0,03	ASTM D7653–10 JIS K0117
Formic acid (HCOOH)	IC	0,001 – 1 0,002 – 0,01	0,003 – 3 0,006 – 0,03	ASTM D7550–09 JIS K0127
	FTIR	0,02 0,01	0,06 0,03	ASTM D7653–10 JIS K0117
Ammonia (NH_3)	IC with concentrator	0,001 – 0.01	0,003 – 0.03	JIS K0127
	FTIR	0,02 0,01	0,06 0,03	ASTM D7653–10 JIS K0117
Total halogenated compounds	IC with concentrator	0,05	0,17	JIS K0101, JIS K0127
Maximum particulate concentration	Gravimetric	0,005 mg/kg	0,015 mg/kg	ASTM D7651–10 JIS Z8813

D.2 Sampling methods

ASTM D7606-11 and ASTM D7650-10 are examples of sampling methods that can be used for the sampling of hydrogen

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