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Hydrogen Fuel — Product Specification — Part 2: PEM fuel cell applications for road vehicles

~~*Carburant hydrogène — Spécification de produit — Partie 2: Applications utilisant des piles à combustible*~~

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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.

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

This Technical Specification provides an initial, albeit incomplete, basis for describing a common fuel to be used by proton exchange membrane (PEM) fuel cell vehicles (FCV) during demonstration programs presently being conducted or envisioned in the near term. A Technical Specification is a normative document that can be published in shorter timeframes than an amendment to a published standard, and it will provide guidance for those who may have to manage small fleets of FCV.

This Technical Specification is intended to consolidate the hydrogen fuel product specification needs anticipated by FCV manufacturers and hydrogen fuel suppliers as both industries proceed toward achieving commercial viability. In this consolidation process, methods to monitor the hydrogen quality that is delivered to these vehicles must also be addressed. Monitoring and controlling hydrogen quality are necessary because specific impurities will adversely affect the fuel cell system and/or on-board H_2 storage system performance. In addition, there may be performance implications in the fuel cell system if certain hydrogen constituent levels are not controlled. A Technical Specification for hydrogen fuel quality can serve as a starting point for all of the participating entities to learn what technology improvements and developments are necessary as well as the impacts of such improvements and developments on commercial viability.

An ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/TS is reviewed after three years to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 14687-2 was prepared by Technical Committee ISO/TC 197, *Hydrogen technologies.*

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

Part 1: All applications except PEM fuel cells for road vehicles, with Technical Corrigenda 1 and 2

Part 2: PEM fuel cell applications for road vehicles

Introduction

This Technical Specification, Part 2 to International Standard ISO 14687:1999, creates two new grades of hydrogen fuel, "Type I, Grade D" and "Type II, Grade D." These new grades are intended to apply to the pre-commercial demonstration of proton exchange membrane (PEM) fuel cell vehicles (FCV) on a limited scale. The purpose of this Technical Specification is to establish hydrogen fuel quality supplied at the above-mentioned scale so that the development of FCV as well as the infrastructure of hydrogen fuel can be implemented in a prompt and efficient manner toward the practical use of FCV. Quality verification requirements shall be determined at the dispenser nozzle or other location by written agreement between the supplier and the customer. Because ISO 14687:1999 includes other grades of hydrogen fuel of lower quality and in the absence of ISO standards for hydrogen fuelling stations and installation of hydrogen equipment, it is important to note that appropriate measures should be taken to prevent cross-contamination of these fuels.

Since the FCV and related technology are developing rapidly, this Technical Specification needs to be revised according to technological progress as necessary. Technical Committee ISO/TC 197, Hydrogen Technologies, will monitor this technology trend. It is also noted that this Technical Specification has been prepared to assist in the development of FCV and related technologies.

Research and development are required to generate specific information so that a final consensus can be reached. These efforts should focus on, but not be limited to:

- PEM catalyst and fuel cell tolerance to hydrogen fuel impurities
- Effects/mechanisms of impurities on fuel cell systems and components
- Impurity detection and measurement techniques for laboratory, production, and in-field operations
- Onboard hydrogen storage technology
- Vehicle demonstration results

Currently, some hydrogen fuel cell vehicle demonstration projects and standard developing organizations are preparing guidelines by issuing technical reports for hydrogen quality based on the current status of fuel cell system and hydrogen production technology. These guidelines will be updated periodically in order to incorporate relevant technology advances, and they will be issued as a series of technical reports as technology matures and is demonstrated. An international standard should be issued only at such time when the aforementioned stakeholders can demonstrate commercial viability and are in agreement that a suitable standard can be written.

Hydrogen Fuel — Product Specification — Part 2: PEM fuel cell applications for road vehicles

1 Scope

This Technical Specification specifies the quality characteristics of hydrogen fuel in order to assure uniformity of the hydrogen product as dispensed for utilization in PEM fuel cell road vehicle systems. All listed constituents of the hydrogen fuel must be measured at or below their individual or class threshold limits as specified in Table 1 of this document.

2 Normative references

The following referenced documents are indispensable for the application 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 14687-1, *Hydrogen fuel — Product specification — Part 1: All applications except PEM fuel cells for road vehicles with Technical Corrigenda 1 and 2*

3 Terms and definitions

For the purposes of this document, the following terms and definitions, in addition to those included in Part 1, apply.

3.1
Constituent
A component (or compound) found within a hydrogen fuel mixture.

3.2
Contaminant
A contaminant is an impurity that adversely affects the components within the fuel cell system or the hydrogen storage system. An adverse effect can be reversible or irreversible.

3.3
Diluent
A diluent is a gaseous, impurity which reduces the concentration of hydrogen, and may be a contaminant or non-reactive in nature.

3.4
Fuel cell system
Power system used for the generation of electricity on a fuel cell vehicle, typically containing the following subsystems: fuel cell stack, air processing, fuel processing, thermal management, water management, and automatic control system.

3.5
Hydrogen fuel index
This is a value based on the subtraction of the summation of the concentration of the Non-hydrogen constituents listed in the table 1 (except Particulates) in this Technical Specification, specifically detected, from 100-volume percent hydrogen.

3.6
Impurity
An impurity is a non-hydrogen constituent in the fuel.

3.7
Impurity level
The concentration of each specific impurity analyzed in a hydrogen fuel. These constituents are commonly measured in μmol/mol with the exception of particulates, which are measured in μgrams/liter and mean particle size in microns (μm).

3.8
Inerts
Non-reactive non-hydrogen constituents, such as nitrogen and gases of the helium group commonly referred to as noble gases including argon, helium, krypton, neon, radon, and xenon. Inert constituents do not contribute to the heating value of the fuel.

3.9
Irreversible Effect
An irreversible effect 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.

3.10
Particulate
A particulate is a solid or aerosol particle, including oil mist, potassium and sodium compounds that may be entrained somewhere in the delivery, storage, or transfer of the hydrogen fuel. Particulates are specified by size (microns) and mass concentration.

3.11
Reversible Effect
A reversible effect 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.

4 Requirements

4.1 Classification

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

a) Type I (grade D): Gaseous hydrogen

b) Type II (grade D): Liquid hydrogen

4.2 Applications

The following information characterizes representative applications of each type and grade of hydrogen fuel. It is noted that suppliers commonly transport hydrogen of a higher quality than some users may require.

Type I, grade D — Gaseous hydrogen fuel for PEM fuel cell road vehicle systems

Type II, grade D — Liquid hydrogen fuel for PEM fuel cell road vehicle 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, are defined in ISO14687-1.

Note 2 There is no equivalent Grade A and B for Type II fuels .

4.3 Limiting characteristics

The directory of limiting characteristics, outlined in Table 1 of this document, specifies the requirements applicable to the aforementioned grades of hydrogen fuel. The methodologies indicated suggest techniques that may be used to ascertain fuel quality. Other methodologies that provide similar measurement capability may be chosen by agreement between the supplier and customer. Means should be provided to test for other contaminants not listed in the table, but identified as potentially harmful to the fuel cell system.

Table 1 — Directory of limiting characteristics

Characteristics (assay)	**Type I** **Grade D**	**Type II** **Grade D**	**Laboratory Test Methods to Consider**
Hydrogen fuel index (minimum, %) [a, b]	99,99	99,99	
Para-hydrogen (minimum, %)	NS	95,0	
Non-hydrogen constituents (maximum content)			Dimensions in micromoles per mole unless otherwise stated
Total gases [b]	100	100	
Water (H_2O)	5	5	ASTM D6348, D5454, (D1946 & D5466)[g]JIS K0225
Total hydrocarbons [c] (C_1 basis)	2	2	EPA T012, T015, ASTM (D1946 & D5466) [g], D6968, JIS K0114
Oxygen (O_2)	5	5	ASTM (D1946 & D5466) [g], JIS K0225
Helium (He), Nitrogen (N_2), Argon (Ar)	100	100	ASTM (D1946 & D5466) [g], JIS K0114
Carbon dioxide (CO_2)	2	2	ASTM (D1946 & D5466)[g], JIS K 0114, K 0123
Carbon monoxide (CO)	0,2	0,2	EPA 25C, ASTM (D1946 & D5466)[g], JIS K 0114, K 0123
Total sulfur compounds [d]	0,004 [f]	0,004 [f]	ASTM (D1946 & D5466) [g], D5504, JIS K 0127
Formaldehyde (HCHO)	0,01	0,01	EPA Method 11, NIOSH 2541, EPA T015, ASTM (D1946 & D5466) [g], JIS K 0114, K 0124, K 0123
Formic acid (HCOOH)	0,2 [f]	0,2 [f]	ASTM (D1946 & D5466) [g], JIS K 0123, K 0127
Ammonia (NH_3)	0,1 [f]	0,1 [f]	ASTM (D1946 & D5466) [g], EPA T015, JIS K 0127
Total halogenated Compounds	0,05	0,05	EPA 200.7, JIS K101
Max Particulates Size [e]	10 µm	10 µm	SCAQMD Method 301-91
Max Particulates Concentration [e]	1 µg/L @ NTP	1 µg/L @ NTP	Gravimetric (EPA IO 3.1)

a. The hydrogen fuel index is the value obtained when the value of Total gases (%) is subtracted from 100 %.

b. The value of Total gases is summation of the values of impurities listed in this table except Particulates.

c. THC may exceed 2 micromole per mole due only to the presence of methane, provided that total gases do not exceed 100 micromole per mole.

d. As a minimum, testing shall include H_2S, COS, CS_2 and Mercaptans, which are typically found in natural gas.

e. Recommended value for Particulates is subject to sampling under realistic operational conditions and improved standardized analytical procedures.

f. These values are based on detection limits of available instrumentation and test methods and serve as a basis for subsequent improvements in test methods and instrumentation. Recommended values for these constituents are subject to additional testing under realistic operational conditions and improved analytical procedures suitable for standardization.

g. A new ASTM standard (WK4548) that will combine relevant portions of these two existing test methods and will utilize gas chromatography/mass spectrometry (GC/MS) to determine trace contaminants in H_2 is under development.

5 Quality Verification

5.1 Hydrogen fuel qualification test

5.1.1 General requirements

Quality verification requirements shall be determined at the dispenser nozzle or other location by written agreement between the supplier and the customer.

5.1.2 Analytical requirements of the qualification tests

The analytical requirements for the qualification tests shall be determined by agreement between the supplier and the customer.

5.1.3 Report results

The detectable limits for analytical methods and instruments used shall be reported along with the results of each test. These detectable limits shall be below the threshold limit for each constituent.

5.2 Lot acceptance tests

Lot acceptance requirements shall be determined by agreement between the supplier and the customer.

6 Test methods

Table 1 lists constituents, their corresponding proposed concentration levels, and test methods (e.g., ASTM, EPA, SCAQMD, JIS) to consider that can detect some of these impurities at levels equal to or below the listed threshold concentrations. Other nationally or internationally accepted test methods may also be used, provided the selected alternative methods are suitable to detect and measure the impurity in question at the same or lower concentration threshold level and if both the user and supplier agree.

All constituents are measured on a molar basis (µmol/mol) except where indicated otherwise. Particulate concentration is measured on a gravimetric basis (µgram/liter) under normal condition (NTP) and the particulate size in microns (µm). Total hydrocarbons are measured on a carbon basis (µmolC/mol).

For the hydrogen fuel index, the value is obtained when the value of the total gases, expressed as mole fraction percent, is subtracted from 100 %. The value of total gases is summation of the values of impurities listed in Table 1 except particulates.

Total hydrocarbons include oxygenated organic species except those specifically listed in Table 1.

For the constituents that are additive, such as total hydrocarbons (THC) and total sulfur compounds, the sum of the constituents are to be less than or equal to ($\leq$) the acceptable limit. The tolerances in the applicable gas testing method are to be the tolerance of the acceptable limit. Note that for the “total” summation compounds such as sulfur, for instance: 0,004 µmol/mol denotes that the summation of the detected sulfur compounds must be less than or equal to 0,004 µmol/mol.

It is recognized within the industry that the preference margin between the lower detectable limit and the acceptable limit for several potential hydrogen constituents is based on the limited state of development of PEM fuel cell technology as of the date of this document. For this document, the best available published standardized analytical methods were chosen. For some constituents, detection techniques with improved repeatability and accuracy levels need to be developed.

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

7 Rationale for Hydrogen Quality Constituents

7.1 Water content

Water (H_2O) generally does not affect the function of 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 micro mole par mole. In addition, it may pose a concern for onboard vehicle fuel system. At the maximum allowable concentration, water will remain gaseous throughout the operating conditions of fuel cell system.

7.2 Total hydrocarbon (THC) content

Different hydrocarbons have different effects on fuel cell performance. Generally aromatic hydrocarbons adsorb more strongly on the catalyst surface than paraffinic molecules thus blocking its access to H_2. The THC or THC compounds are to be tested on a carbon basis. It must be noted that methane (CH_4) is considered inert since its only possible effect is to dilute the hydrogen gas.

7.3 Oxygen content

Oxygen (O_2) in low concentrations is considered an inert impurity, as it does not adversely affect the function of the fuel cell system; however, it may be a concern for onboard vehicle storage systems as it can generate water.

7.4 Helium, nitrogen and argon contents

Inerts, such as helium (He), nitrogen (N_2) and argon (Ar) that do not normally react with fuel cell components or a fuel cell system, are considered non-reactive diluents. Diluents can decrease fuel cell performance and adversely affect system operation.

7.5 Carbon dioxide content

Carbon Dioxide (CO_2) acts largely as a non-reactive diluent. However, it may adversely affect onboard hydrogen storage systems using metal hydride alloys.

7.6 Carbon monoxide content

Carbon Monoxide (CO) is a severe catalyst contaminant. However, the reaction is considered reversible.

7.7 Total sulfur compounds contents

Sulfur containing compounds are considered as severe contaminants causing irreversible performance degradation. The minimum specific sulfur compounds that need to be included in the testing are: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), which may be found in hydrogen reformed from natural gas. However, it is recommended to monitor total sulfur compounds.

7.8 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 is believed to be more severe than that of CO due to slower recovery kinetics.

7.9 Ammonia content

Ammonia (NH_3) causes irreversible performance degradation by contaminating the proton exchange membrane/ionomer and reacting with protons in the membrane/ionomer to form NH_4^+ ions. The threshold value listed is based on available standardized analytical methodology; if more sensitive standardized methodologies become available, revised threshold values should be used after validation.

7.10 Total halogenated compounds contents

Halogenated compounds cause irreversible performance degradation. Sources include chlor-alkali production processes and refrigerants used in processing.

7.11 Particulates

A particulate is a solid that may be entrained somewhere in the delivery, storage, or use of the hydrogen fuel. Particulates are specified by size (microns) and mass concentration. The particulate diameter is specified because of concerns of gasket erosion in tanks, and the particulate quantity is specified to ensure that filters are not clogged and/or particulates do not enter the fuel system and affect operation of valves. Potassium and sodium ions present in aerosols cause irreversible performance degradation by contaminating the proton exchange membrane/ionomer.

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