



ISO/TC 197  
Hydrogen technologies

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ISO 19880-8  
Gaseous hydrogen  
– Fueling stations  
–Hydrogen quality control

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## Introduction

As we approach the start of the proactive development of hydrogen supply infrastructure and market launch of FCVs, it is necessary to establish the requirements and operational protocol for maintaining the quality of hydrogen for FCVs. While ISO 14687-2 sets forth the quality specifications of hydrogen, it does not specify the procedure for administering quality control. As such, this document was prepared to establish an international standard for hydrogen quality control to be followed.

Since the document is required to dictate a practical implementing method for the hydrogen quality control, this standard specifies the minimum analysis work on analytical species and frequency to guarantee the hydrogen quality in ISO 14687-2.

### 1. Scope

This International standard specifies the protocol for ensuring the quality of the gaseous hydrogen quality at hydrogen distribution bases and hydrogen fueling stations for PEM fuel cells for road vehicles.

### 2. Normative references

TBD

### 3. Terms and definitions

#### 3.1.

routine analysis

analysis performed on a periodic basis once every specified time period or once for each lot or batch.

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#### 3.2

non-routine analysis

analysis performed on a non-periodic basis.

#### 3.3

off-line analysis

analysis performed by taking a sample of hydrogen from its flow path into a special sampling cylinder at a hydrogen station or production facility and transferring it to a different location such as an analysis center or an analysis lab of the production facility for analysis.

#### 3.4

nozzle analysis

off-line analysis performed by taking a sample from the end of a dispenser nozzle into a special sampling cylinder at a hydrogen station and transferring it to a different location such as an analysis center or an analysis lab of the hydrogen station for analysis.

#### 3.5

on-line analysis

analysis performed by directing the hydrogen from a branch pipe of its main gas stream (following depressurization for a high-pressure gas) to permanently installed analysis equipment

### 3.6

continuous analysis

on-line analysis performed continuously via an automated system.

## 4. Hydrogen quality

The hydrogen quality shall be consistent with the requirements of ISO 14687-2. For the purpose of this document, the requirements specified under Table 1 of ISO 14687-2 shall be followed.

The rationale for the selection of hydrogen contaminants can be found in Annex A of ISO 14687-2.

Characteristics(assay)	Type I , Type II	Grade D*
Hydrogen fuel index (minimum mole fraction) <sup>a</sup>	99.97%	
Total non-hydrogen gases	300 µmol/mol (ppm)	
Maximum concentration of individual contaminants		
Water (H <sub>2</sub> O)	5	µmol/mol (ppm)
Total hydrocarbons (Methane basis)	2	µmol/mol (ppm)
Oxygen (O <sub>2</sub> )	5	µmol/mol (ppm)
Helium (He)	300	µmol/mol (ppm)
Nitrogen (N <sub>2</sub> ), Argon (Ar) <sup>b</sup>	100	µmol/mol (ppm)
Carbon dioxide (CO <sub>2</sub> )	2	µmol/mol (ppm)
Carbon monoxide (CO)	0.2	µmol/mol (ppm)
Total sulfur compounds (H <sub>2</sub> S basis)	0.004	µmol/mol (ppm)
Formaldehyde (HCHO)	0.01	µmol/mol (ppm)
Formic acid (HCOOH)	0.2	µmol/mol (ppm)
Ammonia (NH <sub>3</sub> )	0.1	µmol/mol (ppm)
Total halogenated compounds ( Halogenate ion basis)	0.05	µmol/mol (ppm)
Maximum particulates concentration	1 mg/kg	

\* Type I (grade D) is gaseous hydrogen fuel for polymer electrolyte membrane (PEM) FCVs.

Type II (grade D) is liquid hydrogen fuel for PEM FCVs.

<sup>a</sup> The hydrogen fuel index is determined by subtracting the “total non -hydrogen gases” in this table, expressed in mole percent, from 100 mole percent.

<sup>b</sup> Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis ( $\mu\text{molC/mol}$ ). Total hydrocarbons may exceed  $2 \mu\text{mol/mol}$  due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed  $100 \mu\text{mol/mol}$ .

<sup>c</sup> As a minimum, total sulphur compounds include  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and mercaptans, which are typically found in natural gas.

<sup>d</sup> Total halogenated compounds include, for example, hydrogen bromide ( $\text{HBr}$ ), hydrogen chloride ( $\text{HCl}$ ), chlorine ( $\text{Cl}_2$ ), and organic halides ( $\text{R-X}$ ).

Source: ISO14687-2 : 2012, Hydrogen fuel – Product specification – Part2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

## 5. Approaches to administration of quality control

### 5.1. Contaminants subject to routine analysis

#### 5.1.1. Approaches to selection of contaminants

Quality control based on the individual contaminants listed in ISO14687-2 is presumed upon clearly identified production, purification and transportation methods of hydrogen. If the hydrogen supply method of a hydrogen station is unclear or unidentified, quality must be assured by analyzing all potential contaminants. Additionally, if multiple supply methods are used for a hydrogen station, constituents to be analyzed must be selected by considering potential sources of contamination for each method to ensure quality.

NOTE The details of production, purification and transportation methods of hydrogen are described in Annex C.

The approach to conducting a quality analysis of the contaminants listed in ISO14687-2 is to first consider the potential sources of contaminants, and, second, establish protocol for analyzing potential contaminants.

#### (1) Potential sources of contaminants

- Sampling procedures
- Characteristics of hydrogen production method(s)
- Characteristics of hydrogen transport method(s)

#### (2) Analysis of possible contaminants

- Possible quantification

### 5.1.2. Routine analysis after hydrogen transportation

#### 5.1.2.1. Storage and transportation of hydrogen in compressed state

When hydrogen produced at a centralized production site is transported by compressing and filling it into transport cylinders, there is no risk that its components are altered by chemical reactions. However, one cannot rule out the possibility of contamination by residual or condensed contaminants that are present in the cylinders in the first place. The risk of contamination is higher when the cylinders, while used exclusively for hydrogen transportation, are used for hydrogen produced from a different feedstock every time, or when the cylinders are new or were recently opened up for inspection.

As a rule, additional routine analyses are deemed unnecessary when the cylinders are used exclusively for FCV hydrogen (compliant with ISO 14687-2), or when the possibility of contamination has been eliminated by repeated purge cycles using FCV hydrogen even if the cylinders were used to transport hydrogen other than FCV hydrogen.

#### 5.1.2.2. Storage and transportation of liquid hydrogen

When hydrogen is transported or stored in liquid state (boiling point of  $-253^{\circ}\text{C}$ ), there is no risk of significant contamination since the hydrogen is purified to a super high level by a PSA or adsorption system upstream of the liquefaction system to prevent any problems caused by solid deposits, regardless of the production method used.

### 5.1.2.3. Pipeline transportation

Pipelines are a potential mode of transportation for hydrogen. When hydrogen is transported via pipelines from a production facility, it is clear that, in general, there is no risk of contamination as demonstrated by the example of city gas transport. Therefore, in principle, no additional routine analyses are required within the pipelines.

### 5.1.2.4. Storage and transportation by storage materials

Storage materials to be packed inside transport cylinders are available in many forms such as metals and organic materials. It is impossible to provide a uniform specification for all variations that include dissolvable materials. As such, the storage material manufacturer's warranty for the quality of the hydrogen end product is to be used as a basis for concluding that the quality of hydrogen has not been altered by the storage material. If it is not possible to demonstrate that there is no risk of contamination of hydrogen due to storage material, a routine analysis of applicable contaminants shall be conducted.

## 5.1.3. Routine analysis after hydrogen production

### 5.1.3.1. Canary species

Canary species is defined by ISO14687-2 as follows: "A 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."

A canary species is a constituent with the highest concentration level in a hydrogen production method. In other words, if it is confirmed that the concentration of the canary species of a given production method is less than its specified limit, other impurities are deemed to have met the standard requirements.

For example, in the case of steam methane reforming (SMR) and pressure swing adsorption (PSA) production and purification, carbon monoxide serves as the canary species.

### 5.1.3.2. Constituents requiring analysis

Analysis is to be conducted on constituents that may contaminate hydrogen regardless of which hydrogen production method is used, as well as those constituents that may contaminate hydrogen due to the unique nature of a given hydrogen production method.

The following is a list of constituents to be analyzed.

Name of constituent	Hydrogen production method to be analyzed	Approach
Nitrogen	All hydrogen production methods	Perform analysis on all production methods since there is a risk of contamination through the equipment
Oxygen	All hydrogen production methods	Same as above
Water	All hydrogen production methods	Same as above

Argon	All hydrogen production methods	Same as above. The ISO standard specifies the limit as a total combined value of nitrogen and argon.
Helium	All hydrogen production methods using natural gas as feedstock	Analysis is necessary since natural gas contains up to 300 ppm of helium. Exclude a hydrogen production method if helium has been removed from the natural gas used for the method.
Ammonia	Ammonia production process generating excess hydrogen Biogas reforming Coal gasification generating hydrogen by-product Ammonia hydride method	
Total halogen	Chloralkali process producing excess hydrogen * Biogas production from plastic waste generating hydrogen Coke oven gas Water electrolysis **	* Excludes ion-exchange-membrane method  ** Limited to cases where tap water is used as feedstock and the performance of water purification system cannot be warranted.
Total sulfur	Steam reforming * Catalytic reforming Partial oxidation Autothermal reforming Coal gasification generating hydrogen by-product Production methods using sulfur compounds as odorant	* Since sulfur compounds are found in the form of H <sub>2</sub> S, analysis of H <sub>2</sub> S, not total sulfur content, is sufficient.
Total hydrocarbons	Production methods in which fossil fuels are present, such as steam reforming, catalytic reforming, partial oxidation, autothermal reforming, and coal gasification generating hydrogen by-product.	
Carbon monoxide	Steam reforming* Catalytic reforming Partial oxidation Autothermal reforming Coal gasification generating hydrogen by-product	
HCHO	Hydrogen production methods using city gas or petroleum as fuel other than steam	Rationale for excluding steam reforming methods using city gas or petroleum: it has been verified that the thermo-equilibrium

	reforming,	concentration of HCHO in steam reforming is significantly lower than the ISO limit.
HCOOH	Hydrogen production methods using city gas or petroleum as fuel other than steam reforming,	Rationale for excluding steam reforming methods using city gas or petroleum: it has been verified that the thermo-equilibrium concentration of HCHO in steam reforming is significantly lower than the ISO limit.

#### 5.1.4. Constituents that do not require analysis

Listed below are constituents for which there is no scientific basis for conducting routine analysis, and the rationale for this conclusion, such as when there is no risk of contamination in any hydrogen production method (a framework is to be provided to conduct non-routine analysis, however):

Substance	Rationale
Hydrogen	While it is clear that hydrogen is the main component, there is no method for directly determining its quantity to a required degree of accuracy. If the proportion of hydrogen is to be calculated by division, it would be necessary to determine the quantity of all contaminants.
All non-hydrogen gases	There is no method for directly determining their quantity. If the proportion of non-hydrogen gases is to be calculated by summation, a qualitative determination of all contaminants would be required.
Particulates	If a filter is installed in the flow path, contamination is highly unlikely. Generally speaking, particulates found at demonstration stations have been lower than the standard upper limit by two digits. Approach to the requirements on particulates will be described in 5.3 below.

#### 5.2. Conditions for conducting non-routine analysis

Irrespective of whether conditions exist for conducting routine analysis described in the preceding section, a non-routine analysis is to be conducted for those constituents deemed necessary if:

- (1) a new production system is constructed at a production site or hydrogen station;
- (2) the production system at a production site or hydrogen station is modified;
- (3) a routine or non-routine open inspection, repair, catalyst exchange, or the like is performed on a production system at the production site or hydrogen station;
- (4) a question concerning quality is raised when, for example, there is a problem with a vehicle because of hydrogen supplied at the production site or hydrogen station, and a claim is received from a user directly or indirectly;
- (5) an issue concerning quality emerges when, for example, a voluntary audit raises the possibility that quality control is not administered properly; or
- (6) analysis is deemed necessary for testing, research or any other purposes.

#### 5.3. Approaches to particulates requirements

As per the requirements of the table in Chapter 3, particulates are to be no more than 1 mg/kg in concentration. According to ISO14687-2, hydrogen is to be sampled from a dispenser nozzle of the hydrogen station under conditions that are as close to the actual fueling conditions as possible. The weight of the particulates collected in a filter is measured.

The filters shall be the ones that can remove 5 micron particulates with a minimum removal efficiency of 99% or the one that has maximum nominal pore size of 5 microns. It shall be installed upstream of the hose breakaway device. This shall filter out the particulate concentration in the hydrogen as per ISO 14687-2.

Note 1: See Annex B for the method of measuring the weight of particulates used at demonstration stations.

Note 2: In fact a filter is also installed in FCVs, and filters installed at both stations and FCVs serve to prevent malfunctioning of FCVs.

## 6. Administration of quality control

### 6.1. Frequency of routine analysis

#### 6.1.1. Routine analysis at a centralized production and distribution facility

As a general rule, the product quality of a plant is consistent regardless of the size of its production system, as long as the input and the operating conditions are consistent. If there are no changes in the input and the operating conditions over a long period of time, only one quality analysis is needed per operation period. The principle of quality control is to perform a daily analysis as defined in 3.1, routine analysis, under 3, Terms and definitions, in order to ease the analytical burden of hydrogen stations and, at the same time, maintain full quality control. However, when the input and the operating conditions have not changed and if it can be assured that the possibility of contamination is eliminated by the good operation and control of the distribution facility by, for example, continuously monitoring the canary species before shipping, the test frequency may be reduced to as low as once per year.

Where the hydrogen generators (such as reformers, water electrolysis apparatus) on the supply side of a distribution facility are operated intermittently and if it can be assured that the possibility of contamination is eliminated by the good operation and control of the distribution facility by, for example, continuously monitoring the canary species following the start of the hydrogen generators, the frequency of analysis may be reduced to as low as once per year.

In this document, the good operation and control means not only that the facility has a continuous analytical instrument installed but also that such analytical equipment is calibrated and otherwise properly maintained to produce appropriate results at all times.

While sampling is to be, as a rule, conducted on the distribution side (transfer side), a separate sampling line may be used as long as it does not raise any quality control issues.

#### 6.1.2. Routine analysis at a hydrogen station

##### 6.1.2.1. Hydrogen stations with off-site supply

Hydrogen received by an off-site hydrogen station is subject to a routine analysis for the chemical constituents that have not been covered by the centralized hydrogen production and distribution facility and for those that may infiltrate the gas after it is accepted by the station. For individual contaminant species that may enter after station acceptance, the frequency of analysis may be reduced to as low as once per year, provided that the possibility of infiltration is deemed eliminated by having a good operation and control program at the station, such as a purge procedure.

While sampling is to be, as a rule, made at the end of a nozzle, it may be conducted upstream of the fueling nozzle to the extent that no changes occur to the quality of hydrogen. (See 7.1)

##### 6.1.2.2. Hydrogen stations with on-site supply

When a hydrogen generator (such as reformer or water electrolysis apparatus) is operated in the daily start and shut mode (DSS), the quality of the hydrogen gas produced fluctuates on a daily basis according to the principle described in 6.1.1. Such operation therefore calls for one analysis per day. As in the case of the centralized production and distribution facilities in 6.1.1, the frequency of analysis may be reduced to as low as once per year, provided that the possibility of infiltration is

deemed eliminated by the good operation and control of the station, such as when accumulators are filled after the canary species is continuously monitored for quality control on a daily basis following the start-up the generator. In this document, the good operation and control means not only that the facility has a continuous analytical instrument installed but also that such analytical equipment is calibrated and otherwise properly maintained to produce appropriate results at all times.

The analysis and monitoring of specific canary species for each hydrogen generator is to be conducted in the same manner as described in 6.1.1.

While sampling is to be, as a rule, made at the end of a nozzle, it may be conducted upstream of the fueling nozzle to the extent that no changes occur to the quality of hydrogen. (See 7.1)

In the case of a station where hydrogen is supplied off-site via pipeline, the use of odorant may be needed. If so, the station will require a deodorant system on-site, and the hydrogen quality needs to be checked downstream of the deodorant system by continuously monitoring the canary species that may originate from such odorant species, as in the case of a hydrogen station with on-site supply.

## 6.2. Administration of analysis and monitoring records

### 6.2.1. Forms for analysis and monitoring records and reports

A typical form used to record and report the analysis and monitoring activities is shown in Annex F. Using Annex F as a reference, each operator is to design and administer forms for records of analyses at its centralized production and distribution facilities, records of sampling and analyses at hydrogen stations, and records of monitoring.

### 6.2.2. Safekeeping and recording

Centralized production or distribution facilities and hydrogen stations are to safekeep their own records of analyses at the facility, of samples collected at the stations, and of monitoring in an appropriate manner.

The records are to be kept for a period of ten years. Such records may be kept at the department (or headquarters) that oversees the operation other than the applicable facilities or stations.

## 7. Routine analysis work

### 7.1. General

Table 7-1 provides the routine analysis work defined on the basis of the attitudes stated in chapter 5 and 6. The table gives the analytical species and the minimum analysis frequencies classified by hydrogen dispensing sites and hydrogen production, purification and transportation methods

Table 7-1 Analytical species and minimum analysis frequencies in routine analysis

Category	Facility type	QC point	Parameter	Standard value	Reduced frequency
Distribution	1. Production of hydrogen from hydrocarbons utilizing steam reforming, catalytic reforming, partial oxidation, or ATR, purification using refining equipment, and distribution	Downstream of the purifier	TS(*1)	0.004 $\mu\text{mol/mol}$	Once a year (*2)
			THC as C <sub>1</sub>	2 $\mu\text{mol/mol}$	Once a year (*2)
			CO	0.2 $\mu\text{mol/mol}$	Once a year (*2)
			N <sub>2</sub> +Ar	100 $\mu\text{mol/mol}$	Once a year (*2)
			H <sub>2</sub> O	5 $\mu\text{mol/mol}$ (dew point $\leq -66^\circ\text{C}$ )	Once a year (*2)
	2. Electrolysis of NaCl for hydrogen; purification; and distribution	Downstream of the refiner	O <sub>2</sub>	5 $\mu\text{mol/mol}$	Once a year (*2)
			Halogen	0.05 $\mu\text{mol/mol}$	Once a year (*2)
			N <sub>2</sub> +Ar	100 $\mu\text{mol/mol}$	Once a year (*2)
	3. Purification of coke-oven gas; distribution	Downstream of the refiner	H <sub>2</sub> O	5 $\mu\text{mol/mol}$ (dew point $\leq -66^\circ\text{C}$ )	Once a year (*2)
			O <sub>2</sub>	5 $\mu\text{mol/mol}$	Once a year (*2)
			TS	0.004 $\mu\text{mol/mol}$	Once a year (*2)
			THC as C <sub>1</sub>	2 $\mu\text{mol/mol}$	Once a year (*2)
			CO	0.2 $\mu\text{mol/mol}$	Once a year (*2)
			Halogen	0.05 $\mu\text{mol/mol}$	Once a year (*2)
			N <sub>2</sub> +Ar	100 $\mu\text{mol/mol}$	Once a year (*2)
			NH <sub>3</sub>	0.1 $\mu\text{mol/mol}$	Once a year (*2)
			HCHO	0.01 $\mu\text{mol/mol}$	Once a year (*2)
			HCOOH	0.2 $\mu\text{mol/mol}$	Once a year (*2)
	4. Purification of byproduct hydrogen from ethylene plants; distribution	Downstream of the refiner	TS	0.004 $\mu\text{mol/mol}$	Once a year (*2)
			THC as C <sub>1</sub>	2 $\mu\text{mol/mol}$	Once a year (*2)
CO			0.2 $\mu\text{mol/mol}$	Once a year (*2)	
N <sub>2</sub> +Ar			100 $\mu\text{mol/mol}$	Once a year (*2)	
H <sub>2</sub> O			5 $\mu\text{mol/mol}$ (dew point $\leq -66^\circ\text{C}$ )	Once a year (*2)	
O <sub>2</sub>	5 $\mu\text{mol/mol}$	Once a year (*2)			

Category	Facility type	QC point	Parameter	Standard value	Reduced frequency
Station	1. With off-site supply of transported compressed or liquid hydrogen	End of nozzle	Those not analyzed by the distributor		Once a year (*2)
			N <sub>2</sub> +Ar	100μmol/mol	Once a year (*2)
			H <sub>2</sub> O	5μmol/mol (dew point ≤ -66°C)	Once a year (*2)
			O <sub>2</sub>	5μmol/mol	Once a year (*2)
	2. With off-site supply from hydrogen pipelines	Downstream from odorant	(Those listed for the odorant)		Once a year (*2)
			Those not analyzed by the distributor		Once a year (*2)
		End of nozzle	CO	0.2μmol/mol	Once a year (*2)
			N <sub>2</sub> +Ar	100μmol/mol	Once a year (*2)
			H <sub>2</sub> O	5μmol/mol (dew point ≤ -66°C)	Once a year (*2)
			O <sub>2</sub>	5μmol/mol	Once a year (*2)
	3. With on-site supply of hydrogen produced from hydrocarbons utilizing steam reforming, catalytic reforming, partial oxidation, or ATR, and purification using refining equipment	Downstream of the refiner	CO	0.2μmol/mol	Continuous and once/year (*2) (*4)
			TS	0.004μmol/mol	Once a year (*2)
		End of nozzle	THC as C <sub>1</sub>	2μmol/mol	Once a year (*2)
			CO	0.2μmol/mol	Once a year (*2)
			N <sub>2</sub> +Ar	100μmol/mol	Once a year (*2)
			H <sub>2</sub> O	5μmol/mol (dew point ≤ -66°C)	Once a year (*2)
	O <sub>2</sub>	5μmol/mol	Once a year (*2)		
	4. With on-site supply from hydroelectrolysis, and purification using refining equipment	Downstream from the refiner	O <sub>2</sub>	5μmol/mol	Continuous and once/year (*2)
			H <sub>2</sub> O	5μmol/mol (dew point ≤ -66°C)	Continuous and once/year (*2)
		The end of nozzle	Halogen	0.05μmol/mol	Once a year (*2)
N <sub>2</sub> +Ar			100μmol/mol	Once a year (*2)	
H <sub>2</sub> O			5μmol/mol (dew point ≤ -66°C at atmospheric pressure)	Once a year (*2)	
O <sub>2</sub>			5μmol/mol	Once a year (*2)	

[Use of diligence in looking at Table 7-1]

\*1 The minimum frequency of the analysis is premised on the combination of continuous analysis of the canary species (CO for hydrocarbon cracking and O<sub>2</sub>/H<sub>2</sub>O for water electrolysis) and proper operation controls to make sure no mixing of impurities will occur. If that premise is not satisfied, the analysis shall be carried out once a day.

\*2 Since sulfur in steam reforming is mostly found as hydrogen sulfide (H<sub>2</sub>S), H<sub>2</sub>S analysis may be performed in lieu of total sulfur analysis.

\*3 The batch analysis once a year is needed even if a continuous analysis is performed.

\*4 If the hydrogen on a pipeline contains odorant, the odorant shall be analyzed with minimum frequency of once a year.

## **7.2. Sampling at the hydrogen station**

Analytical methods are divided into on-line analyses and off-line analyses. For the off-line analyses, sampling needs to be performed at the hydrogen station.

As a rule, the sampling is to be done at the end of the dispenser nozzle. A sampling line, which is installed separately, may be used as long as it does not raise any quality control issues. This Chapter will cover both types of sampling methods.

A container dedicated for analytical sampling should be employed as a specific means to prevent contamination at the time of sampling.

## **7.3. Maintenance of analytical equipment**

The analytical equipment of a centralized production and distribution facility or hydrogen station are to be properly maintained in accordance with the respective user manual and operating instructions at the responsibility of the operator.

## Annex A Hydrogen analysis methods

The table below shows the analytical methods for the impurities in hydrogen (source: ISO-154687-2). See Annex A for the details of each analytical method.

Table A-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 <sub>2</sub> O)	Dewpoint analyzer	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 analyzer	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 <sub>2</sub> )	Galvanic cell O <sub>2</sub> 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
Nitrogen (N <sub>2</sub> ). Argon (Ar)	GC/MS with jet pulse injection	5 (N <sub>2</sub> ), 1 (Ar) 0.03	15 (N <sub>2</sub> ), 3 (Ar) 0.1	ASTM D7649-10 JIS K0123
	GC/TCD	1 – 3	3 – 10	JIS K0114

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
	GC/PDHID	0.001	0.01	JIS K0114
Carbon dioxide (CO <sub>2</sub> )	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 <sub>3</sub> )	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. K0127
Maximum particulate concentration	Gravimetric	0.005 mg/kg	0.015 mg/kg	ASTM D7651-10 JIS Z8813

Remarks:

GC/MS: Gas Chromatography/Mass Spectrometry

FTIR: Fourier Transform Infrared Spectroscopy  
FID: Flame Ion Detector  
GC/FID: Gas Chromatography/ Flame Ion Detector  
GC/PDHID: Gas Chromatography/ Pulsed Discharge Helium Ionization Detector  
GC/TCD: Gas Chromatography/ Thermal Conductivity Detector  
IC: Ion Chromatography  
GC/SCD: GC/FID: Gas Chromatography/ Sulfur Chemiluminescence Detector  
DNPH/HPLC: Dinitrophenylhydrazine/ High performance liquid chromatography

Reference : ISO14687-2 : 2012, Hydrogen fuel – Product specification – Part2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

## Annex B Analysis of particulates

### B-1 Analysis

Catch the particulates from product hydrogen by filter (Teflon; aperture of 0.2  $\mu\text{m}$ ) and measure the weight by scale in the following steps:

- (1) Preparation: Dry the filter and filter holder well and measure their weight using a scale.
- (2) Connect a high-pressure buffer tank to the dispenser nozzle via a receptacle. Fill a predetermined amount of hydrogen (an amount of 2 kg or more is desirable to minimize error) at high pressure.
- (3) Disconnect the buffer tank from the dispenser nozzle for measurement.
- (4) Set the secondary pressure of the buffer tank to 1 MPa or below using the secondary pressure-regulating valve, and feed the hydrogen through the filter at a constant flow rate using a rotameter.
- (5) Remove and dry the filter and filter holder well to measure them using a scale.

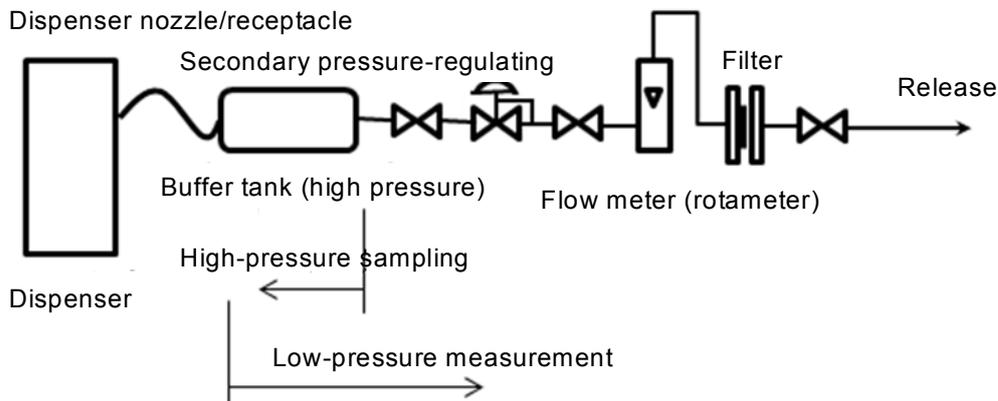


Figure B-1 Flow diagram of measurement system for particulates in product hydrogen

## Annex C Methods of hydrogen production, purification and transportation

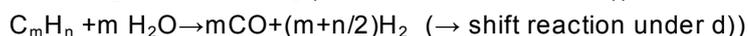
The process of hydrogen supply is divided into the following stages: (i) production, in which hydrogen is produced by chemical reactions or other means; (ii) purification, in which the purity of hydrogen is increased; and (iii) transportation, in which hydrogen is transported to consumption areas or other destinations, if needed. The following is a list of hydrogen production, purification, and transportation methods that fall within the scope of this document. The list includes those methods that are still in the research stage but have the potential for commercial and practical use in the future.

### C.1 Hydrogen production methods

#### a) Steam reforming (off-site/on-site)

Feedstock: includes petroleum hydrocarbons such as natural gas, city gas, LPG, naphtha, and kerosene, as well as oxygenated hydrocarbons such as alcohol and dimethyl ether (DME).

Reaction:  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$  ( $\rightarrow$  shift reaction under d))



This is the most commonly used method for producing hydrogen from feedstocks such as natural gas, petroleum and other hydrocarbons, as well as methanol. At oil refineries and petroleum chemical plants, large-scale production units of this kind are used for on-site processes. At on-site hydrogen stations, small steam reforming units are used to produce hydrogen from feedstocks such as city gas, LPG and naphtha. In addition to hydrogen, a large amount of carbon monoxide and other by-products are generated; as such, it is common practice to install additional systems downstream for increasing the amount of hydrogen by shift reactions or other means. Since reforming catalysts are deactivated by sulfur content, the feedstock is desulfurized to an allowable level in advance.

#### b) Partial oxidation (off-site)

Feedstock: Fossil fuels, alcohol, plastic waste, etc.

Reaction:  $\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$  ( $\rightarrow$  shift reaction under d))

This method produces hydrogen by partially combusting (oxidizing) fossil fuels such as natural gas, petroleum and coal by using atmospheric air or oxygen. Large production units are used commercially to produce syngas or hydrogen for power generation and chemical feedstocks. In addition to hydrogen, a large amount of carbon monoxide and other by-products are generated; as such, it is common practice to install additional systems downstream for increasing the amount of hydrogen by shift reactions or other means. The sulfur content is removed from the feedstock or after the gas is partially oxidized.

#### c) Autothermal reforming (off-site)

Feedstock: Fossil fuels, alcohol, plastic waste, etc.

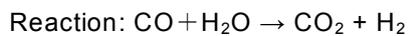
Reaction:  $\text{CH}_4 + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} \rightarrow \text{CO} + 2.5\text{H}_2$  ( $\rightarrow$  shift reaction under d))

This hydrogen production method combines steam reforming and partial oxidation. Because steam

reforming is endothermic, it requires external heat supply. By contrast, partial oxidation takes place independently since it is exothermic. Autothermal reforming combines the two methods in a manner that properly achieves heat balance. In addition to hydrogen, a large amount of carbon monoxide and other by-products are generated; as such, it is common practice to install additional systems downstream for increasing the amount of hydrogen by shift reactions or other means. Since catalysts are deactivated by sulfur content, the feedstock is desulfurized to an allowable level in advance.

d) Water gas shift reaction (WGSR)

Applicable gas: gas containing a high concentration of carbon monoxide such as coke oven gas and the resultant gases of steam reforming, partial oxidation, or autothermal reforming.



The WGSR is the second stage of hydrogen production process. The method further increases the amount of hydrogen by catalytically reacting water with carbon monoxide, which is found in the so-called syngas (gas mixture of hydrogen and carbon monoxide) produced by one of the methods described under a) to c) above, or in the coke oven gas produced by the method described under f) below. The WGSR is commonly used as the second stage of steam reforming of all scales from small to large. However, since a stoichiometric amount of carbon dioxide is always produced as a by-product, the WGSR alone is not able to generate high-purity hydrogen and a purification unit that separates hydrogen and carbon dioxide must be installed downstream. Since it is an equilibration reaction, in some cases the WGSR is conducted in the two stages of high temperature shift and low temperature shift employing different catalysts, in order to increase the reaction level.

e) Catalytic reforming (off-site)

Feedstock: Desulfurized heavy naphtha



This method is used to produce aromatic compounds through the cyclization and dehydrogenation of the heavy naphtha in petroleum (with about six to eleven carbon atoms). The aromatic compounds are used as high-octane gasoline base materials and benzene, toluene, and xylene (BTX). The reaction also produces hydrogen as a by-product and is used commercially at petroleum refineries and petroleum chemical industries. Since hydrogenolysis occurs as a side reaction, the hydrogen purity is at approximately 75 to 85% after reformed naphtha, the main liquid product, is separated into gas and liquid. The rest consists mainly of lower saturated hydrocarbons. Since reforming catalysts are deactivated by sulfur content, the heavy naphtha is desulfurized to an allowable level in advance. While the by-product hydrogen from catalyst reforming is consumed internally for reactions at many facilities, some of it is purified further for commercial sale.

f) Coke-oven gas (COG) (off-site)

Feedstock: coal, high-temperature \*hot-COG: method for increasing the amount of hydrogen by shift reactions

Reaction:

Generally speaking, coal is employed for iron ore reduction. When the coal is carbonized in a coke oven, coke-oven gas (COG) is produced as a by-product. Hydrogen accounts for about 55% of the

total content of COG, while carbon monoxide and other coal-derived impurities make up the rest. Cold-COG is achieved by removing these non-hydrogen components and is used as fuel on-site. Some Cold-COG is further purified by adsorption and deoxidation/dehumidification and the resultant hydrogen is distributed commercially for industrial use. The Hot-COG method is used to amplify the amount of hydrogen by the shift reaction of COG, but it has yet to be deployed in large-scale systems.

In the steel industry, blast furnace gas (BFG) and Linz-Donawitz converter gas (LDG) are also produced as by-products. While the hydrogen purity is less than 10%, the concentration of carbon monoxide is high. As a result these by-products may be used as shift reaction feedstocks for the Hot-COG method.

g) Steam cracking for ethylene by-product (off-site)

Feedstock: fossil fuels

Reaction:

At petrochemical plants, light naphtha and petroleum distillates are thermally cracked using high-temperature steam (steam cracked) to produce polyethylene or polypropylene, the most common plastics. During the process a gas mixture consisting of hydrogen and methane is produced as a by-product. While the hydrogen purity of this gas mixture varies significantly from 10 to 70%, in some cases hydrogen is further purified by such means as adsorption and is distributed for industrial use. In addition to the above, hydrogen is also generated as a by-product by styrene production through ethylbenzene dehydrogenation or by cyclohexanone production through cyclohexanol dehydrogenation.

h) Chloralkali process (off-site)

Feedstock: brine, electricity

Reaction:  $2\text{H}_2\text{O} + 2\text{NaCl} \rightarrow 2\text{NaOH} + \text{Cl}_2 + \text{H}_2$  (overall cell reaction)

Using sodium chloride and water as feedstocks, chloralkali process produces sodium hydroxide, chlorine, and hydrogen. Also called electrolytic soda process, the method can be categorized into different techniques, such as the membrane cell process and mercury cell process. However, the ion-exchange-membrane process is widely employed from the viewpoint of environmental issue. In general, sodium hydroxide or sodium hydroxide and chlorine ( $\text{NaOH}+\text{Cl}_2$ ) are the main products generated to meet their demand while hydrogen is produced merely as a by-product. By-product hydrogen is utilized within business premises or at nearby factories, but in many cases it is shipped to other locations and distributed for industrial use.

i) Electrolysis of water (off-site/on-site)

Feedstock: water and electricity

Reaction:  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$  (overall cell reaction)

This method decomposes water into oxygen and hydrogen via electrolysis. Different techniques are available, including alkaline water electrolysis, polymer electrolyte membrane electrolysis, and solid oxide electrolysis (steam electrolysis). While the method has not yet been deployed at many large plants, it is considered a highly promising method for producing hydrogen from solar, wind and other

renewable sources of energy. Small units for the on-site production of pure hydrogen for industrial use are widely deployed, and is a possible candidate for hydrogen stations.

## C.2 Hydrogen purification methods

### a) Adsorption

Applicable gas: hydrogen of 50 to 99.9% purity

This method takes advantage of the property of molecules with high polarity to be adsorbed on solid surfaces to remove carbon monoxide and other contaminants within hydrogen. When hydrogen is passed through an adsorption column, only hydrogen, which has low polarity, is obtained at the outlet. Since the adsorbent filled in the column eventually reaches a breakthrough point due to contaminant build-up, desorption is performed from time to time. In the desorption process, impurities are removed by either reducing the pressure and/or increasing the temperature than that of adsorption. The adsorption method where pressure is altered is called Pressure Swing Adsorption (PSA) while the one where temperature is changed is called Temperature Swing Adsorption (TSA). The method that uses both pressure and temperature is called Pressure Temperature Swing Adsorption (PTSA). For hydrogen purification, PSA is used widely.

The purge gas used to remove impurities from the column by the desorption process contains hydrogen, which is lost from the total amount of recovered hydrogen. By having multiple columns with time lags in the absorption/desorption processes, a continuous purification treatment becomes possible. PSA is commonly used downstream of steam reforming or shift reactions in oil refineries to reduce the carbon monoxide purity to 20 ppm or below. Because a PSA system is sometimes installed in multiple stages to remove impurities to a specified concentration, there is a tradeoff between the purity level and the recovery rate. PSA is also used downstream of small stream reforming systems at hydrogen stations and has a wide range of small- to large-scale commercial applications.

When COG is purified using PSA, traces of oxygen may remain. Therefore catalytic combustion (Pd or Ni–La<sub>2</sub>O<sub>3</sub>–Rh, etc.) is performed for deoxidation, and any moisture generated is removed by a dehumidifier (dehumidification process).

### b) Membrane separation

Applicable gas: hydrogen of approx. 50 to 90% purity

In principle, membrane separation for hydrogen purification consists of a method that takes advantage of the fact that the molecular size of hydrogen is smaller than the molecular sizes of impurities and another method that permeates hydrogen using a material that performs a dissociative adsorption of only hydrogen molecules (returns to hydrogen molecules on the other side of the membrane). The former has been deployed commercially on a large scale using polyimide hollow fiber membranes. For the latter, palladium and other precious metals are used, but large-scale commercial application is still under research and development. There is a tradeoff between the purity level and the recovery ratio, but the latter method has a higher recovery ratio.

c) Solvent absorption

Applicable gas: Shift gas (hydrogen and carbon dioxide mixture gas)

This method uses a solvent to absorb carbon dioxide to separate hydrogen from the gas mixture of hydrogen and carbon dioxide generated by a shift reaction. It was the leading hydrogen purification method before PSA became the mainstream method. To this date there are many large-scale plants employing the solvent absorption method. While the hydrogen purity is generally about 95% and a large amount of heat energy is required for the regeneration of the solvent (i.e., the release of carbon dioxide), the method allows for the recovery of carbon dioxide at a relatively high purity, a benefit not available with the PSA method. Depending on the type of solvent used, the method is classified as the chemical absorption method that uses amine, potassium carbonate aqueous solution or the like, or the physical absorption method that uses polyethylene glycol (PEG), methanol or the like.

d) Cryogenic separation

Applicable gas: high purity hydrogen

This method takes advantage of the differences in boiling points between hydrogen and other molecules to cause a phase separation at low temperatures, turning hydrogen into gas and impurities into liquid. There are very few cases where this method is employed with hydrogen purification as the main goal; instead, it is largely used to separate hydrogen during a continuous production of carbon monoxide. Additionally, when hydrogen is liquefied to improve transportation efficiency, it may sometimes go through cryogenic separation during the cooling stage in the liquefaction process.

e) Methanation

Applicable gas: a hydrogen-rich gas mixture containing traces of carbon monoxide and carbon dioxide following a primary purification process

Reaction:  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$

This method is employed to catalytically reduce carbon monoxide and carbon dioxide remaining in hydrogen in traces into methane and is usable when the allowable concentration level of methane is higher than that of carbon monoxide. The process is the reverse reaction of steam reforming, and is thus unusable unless the fractions of carbon monoxide and carbon dioxide in the gas have been reduced by primary purification. At some oil refineries and other hydrogen production plants, this process is added downstream of steam reforming, shift reaction, and solvent absorption.

f) Selective CO oxidation

Applicable gas: a hydrogen-rich gas mixture containing traces of carbon monoxide dioxide following a primary purification process

Reaction:  $\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$

This method is used to catalytically convert the trace amounts of carbon monoxide remaining in hydrogen into carbon dioxide by introducing oxygen and is usable when the allowable concentration level of carbon dioxide is higher than that of carbon monoxide. Special catalysts and reaction

conditions are selected so that oxidation does not cause hydrogen to combust. While the method is used to purify hydrogen for small stationary fuel cell systems, it has not been deployed for large-scale commercial systems.

### C.3 Hydrogen transportation methods

#### Transportation of hydrogen in compressed form

Hydrogen produced and purified at a central production facility is compressed and then filled into gas cylinders, bundles or other transport containers and shipped to off-site stations by hydrogen loaders and hydrogen trailers. Steel cylinders are pressurized to 14.7 MPa or 19.6 MPa, and composite cylinders to 35 MPa or 45 MPa. No odorant is necessary. The cylinders are kept at hydrogen stations and are pressurized by a compressor if needed.

#### Transportation of hydrogen in liquid form

Hydrogen (boiling point:  $-253^{\circ}\text{C}$ ) produced and purified at a centralized production facility is cooled to a liquid form using liquefied nitrogen and liquefied natural gas (LNG), among other things. The liquefied hydrogen is then filled into cylinders on special tanker trucks and trailers to be shipped to off-site stations. Odorization is not required. At hydrogen stations, the liquefied hydrogen is unloaded and kept in special storage tanks. After going through an evaporator, the hydrogen is dispensed in a compressed state, or is transferred by pumps in a liquefied state. Liquid hydrogen has been used commercially in lieu of compressed hydrogen for transportation.

#### Pipeline transportation

Pipeline transportation is looked upon as a future method of hydrogen transportation. Hydrogen produced and purified at a centralized production site is forwarded to pipelines and transported to an off-site hydrogen station. The same method is used for city gas transportation. Different approaches are considered, including the one using pipelines installed exclusively for hydrogen, and another using the city gas pipelines to transport hydrogen and city gas as a gas mixture. At this point in time the former approach is not yet used extensively but is only considered as a future possibility since pipelines dedicated to hydrogen transportation are only installed in special demonstration areas or industrial areas. Because the pipelines would pass through residential and city centers, odorization may be required. In that case, new impurities derived from odorants would infiltrate during transport. In general, odorants are made of mercaptan, sulfide, and cyclohexene, indicating a possibility of contamination by total sulfur content and/or total hydrocarbons. Since the pipeline pressure is set higher than ambient pressure, no contaminants would enter from the atmosphere.

The hydrogen transported via dedicated, odorized pipelines is deodorized at hydrogen stations and pressurized by a compressor. When transported with city gas, the gas mixture goes through a hydrogen separation process and is pressurized by a compressor.

In North America and Europe, hydrogen pipelines extending a few hundred kilometers are already in operation.

#### Transportation by storage materials

Storage materials are filled into storage cylinders and cartridges for hydrogen transportation. Once

transported to hydrogen stations, the cylinders are regulated under specified conditions (temperature, pressure, etc.) to release hydrogen, and the hydrogen is compressed once it is released.

#### Other transportation methods

Methods using organic hydride and ammonia hydride involve chemical reactions before the quality of hydrogen is set. For quality control purposes, these methods are not considered valid hydrogen transportation methods.