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Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles

Combustible à base d'hydrogène — Méthodes analytiques — Applications utilisant des piles à combustible à membrane échangeuse de protons (PEM) pour véhicules routiers

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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.

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

This document was prepared by Technical Committee ISO/TC 158, *Gas analysis*. with the collaboration of ISO/TC 197, *Hydrogen technologies* to complete the collection of standards related on H_2 quality.

Introduction

The hydrogen supply infrastructure for Fuel Cell Electric Vehicles requires specifications and an operational protocol for maintaining the quality of the hydrogen used to fuel the vehicles. To fulfill these requirements, several documents were written: ISO 14687 which sets forth the quality specifications of hydrogen, and ISO 19880-8[1] which is specifying the quality assurance and control protocol for ensuring them. There was still a need for developing a standard on analytical methods to measure the level of contaminants found in the gaseous hydrogen fuel. The development and validation of these analytical protocols is necessary in order to assure the hydrogen quality required by ISO 14687 sets for permeating commercialized FCVs and hydrogen infrastructure in the market. This document sets criteria to validate the analytical methods used for the quality control at hydrogen distribution facilities.

Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles

1 Scope

This document specifies the validation protocol of analytical methods used for ensuring the quality of the gaseous hydrogen quality at hydrogen distribution bases and hydrogen fueling stations for PEM fuel cells for road vehicles. Recommendation on calculation of uncertainty budget is also given in this document.

This protocol is established mainly for analysis done in laboratories after the sampling of hydrogen either at hydrogen distribution bases or at hydrogen refueling stations. The specific requirements for on-line monitoring are not covered by this document.

A list of suitable analytical techniques used to measure each impurity in hydrogen, according to the specification defined by ISO 14687, is also given in this standard

Moreover, recommendations for keeping the integrity of the sample are also given in order to ensure the quality of the measurement.

Guideline for reporting the analytical results is also included in this standard.

2 Normative references

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

ISO 14687, *Hydrogen fuel — Product specification*

ISO 19880-1, *Gaseous hydrogen — Fueling stations — Part 1: General requirements*

3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols

B	absolute bias
b	relative bias in %
k_Q	multiplier used in calculating limit of quantification
m	number of replicate observations used during the validation of analytical method

n	number of replicate observations averaged when reporting results
R	relative recovery (apparent recovery) in %
R'	relative spike recovery in %
s	standard deviation
s_0	estimated standard deviation of single results at or near zero concentration
s'_0	standard deviation used for calculating an LOD or LOQ
s_r	repeatability standard deviation
s_R	reproducibility standard deviation
u	standard uncertainty
x_{CRM}	reference value of the Certified Reference Material
x_{mean}	mean value (arithmetic average)
x_{ref}	reference value
x'_{blank}	mean value of the unspiked sample in a recovery experiment
x'_{mean}	mean value of spiked sample in a recovery experiment
x_{spike}	added concentration in a recovery experiment

5 Limit characteristics of the Fuel

The quality specifications of hydrogen fuel dispensed to PEM fuel cells for road vehicles are listed in ISO 14687. The fuel quality requirements at the dispenser nozzle applicable to the hydrogen fuel for PEM fuel cells in road vehicles shall meet the requirements of grade D of this standard.

6 Requirements for analytical method validation and fit for purpose

6.1 Generalities

Method validation for fit of purpose is basically the process of defining the application requirements, and confirming that the method under consideration has capabilities consistent with what the application requires. The method performance characteristics (Table 1) that are associated with method validation shall be evaluated. Using the information coming from the validation, the laboratory shall determine if the method is suitable for the analysis of impurities in H_2. Criteria are defined for establishing the fit for purpose of the developed method. If the method doesn't fulfil these criteria, it cannot be used for the analysis of impurities in H_2; another method shall be used.

A laboratory may adopt a validated procedure which, e.g. has been published as a standard, or buy a complete measuring system to be used for a specific application from a commercial manufacturer. In both these cases, basic validation work has already been carried out but the laboratory shall confirm its ability to apply the method. It means that some experimental work shall be done to demonstrate that the method works in the end-user's laboratory. The laboratory shall also determine if the method is suitable for the analysis of impurities in H_2.

6.2 Characteristic for analytical methods

The list of the main characteristics commonly evaluated during method validation is given in Table 1.

Table 1 — Overview of characteristics for analytical methods

Performance characteristic	Section
Selectivity	6.2.1
Limit of detection (LOD) and limit of quantification (LOQ)	6.2.2
Working range	6.2.3
Trueness bias, recovery	6.2.4
Precision repeatability, intermediate precision and reproducibility	6.2.5
Measurement uncertainty	6.2.6
Ruggedness (robustness)	6.2.7

6.2.1 Selectivity

6.2.1.1 Definition and estimation

Analytical selectivity relates to "the extent to which the method can be used to determine particular analyte in mixtures or matrices without interferences from other components of similar behaviour"[2].

The selectivity of a method is usually investigated by studying its ability to measure the analyte of interest in samples to which specific interferences have been deliberately introduced (those thought likely to be present in samples).

6.2.1.2 Fit for purpose for H_2 analysis

The selectivity is acceptable if:

— the effect of interferences is examined by the analysis of test samples containing various suspected interferents in the presence of analytes of interest;

— the presence of suspected interferents doesn't inhibit detection or quantification of the analytes;

— the presence of suspected interferents doesn't increase the uncertainty of the measurements.

If detection or quantification is inhibited by interferences, further method development is required or another method shall be used.

In the case of impurities in hydrogen, the interferences with the other impurities specified in ISO 14687 have to be investigated. If other impurities not specified could have an effect on the measurement, they shall be studied also.

6.2.2 Limit of detection and limit of quantification

6.2.2.1 Definition and calculation

It is necessary to distinguish between the instrument detection limit and the method detection limit. The instrument detection limit can be based on the analysis of a sample, often a blank, presented directly to the instrument (i.e. omitting any sample preparation steps), or on the signal to noise ratio in, e.g. a chromatogram.

To obtain a method detection limit, the LOD shall be based on the analysis of samples according the whole measurement procedure (including sample preparation or preconcentration) and calculated with the same formula as for the test samples.

The determination limit or limit of quantification (LOQ) is the lowest amount of analyte in a sample that can be quantitatively determined with a stated acceptable precision and accuracy, under stated experimental conditions. Depending on the degree of rigour needed or the level of risk that can be tolerated, the LOQ is typically 4-20 times the standard deviation of a low level sample or blank measurement[3].

The suitable samples for estimating LOD and LOQ should preferably be:

a) blank samples, i.e. matrices containing no detectable analyte;

b) test samples with concentrations of analyte close to expected LOD.

Blank samples work well for methods where a measurable signal is obtained for a blank, such as spectro-photometry and atomic spectroscopy. However, for techniques such as chromatography, which rely on detecting a peak above the noise, samples with concentration levels close to or above the LOD are required. These can be prepared by spiking a blank sample.

The standard deviation s_0 is normally obtained under repeatability conditions. It is important that this standard deviation was representative of the precision obtained for typical test samples, and that sufficient replicate measurements are made to give a reliable estimate. The number of replicates (m) should be between 6 and 15 to give representative value; 10 replicates are often recommended in validation protocols. The standard deviation s_0 is obtained by the following Formula (1).

$$s_0 = \sqrt{\sum \left(x_i - x_{\text{mean}}\right)^2 / \left(m-1\right)} \tag{1}$$

where

x_i is the measurement i;

x_{mean} is the average value;

m is the number of replicates used during validation of analytical method.

In many measurement procedures the mean of n replicates is reported in routine use of the method, where each replicate is obtained by following the entire measurement procedure. In this case the standard deviation of single results s_0 should be calculated by dividing with the square root of n, where n is the number of replicates averaged in routine use following the Formula (2):

$$s'_0 = s_0 / \sqrt{n} \tag{2}$$

Both LOD and LOQ are normally calculated by multiplying the standard deviation s'_0 by a suitable factor k_Q[9]. The LOD is calculated using the Formula (3):

$$LOD = 3 \times s'_0 \tag{3}$$

LOQ is calculated using Formula (4):

$$LOQ = 10 \times s'_0 \tag{4}$$

The IUPAC default value for k_Q is 10[9] and if the standard deviation is assumed to be constant at low concentrations this multiplier corresponds to a relative standard deviation (RSD) of 10 %. The multiplier k_Q could be also equal to 5 or 6 which corresponds to RSD values of 20 % and 17 % respectively.

This will be sufficient if an estimate of LOD/LOQ is required simply to demonstrate that the concentrations of samples will be well above the LOD/LOQ. Where laboratory samples are expected to contain low concentrations of the analyte, the LOD/LOQ should be monitored on a regular basis. This could be the case for the impurities at lowest concentrations where LOQ could be close to the specification value (for example sulphur analysis).

6.2.2.2 Fit for purpose for H_2 analysis

The quantification limit of the analytical method shall be below the threshold value in order to be able to quantify the impurity in the sample. The criterion for acceptation is presented in Formula (5):

$$LOQ + u_{\mathrm{LOQ}} < \text{threshold value} \tag{5}$$

where u_{LOQ} is the uncertainty at the LOQ concentration.

The detection limit and determination limit should be determined only if they are close to the threshold limit requested in ISO 14687 for H_2 grade D.

6.2.3 Working range

6.2.3.1 Definition and calculation

The 'working range' is the interval over which the method provides results with an acceptable uncertainty[3].

The lower end of the working range is generally bounded by the limit of quantification LOQ. This lower end can also be defined by the concentration of the lower calibration standard used during the validation of the method.

The upper end of the working range is defined by concentration at which significant anomalies in the analytical sensitivity are observed (end of model linearity or saturation of the signal). This upper end can also be defined by the concentration of the upper calibration standard used during the validation of the method.

Between the LOQ and the upper end of the instrument working range, the response of the instrument obeys a known relationship, e.g. linear, curvilinear etc. During validation it shall be necessary to:

a) calibrate the analyser using calibration mixtures with defined uncertainties and precision , taking into account conversion factor if necessary. For example, use calibration gas mixtures prepared by gravimetry (see ISO 6142[4]) or by dynamic methods (see ISO 6145- series[5]);

b) establish this relationship.

6.2.3.2 Fit for purpose for H_2 analysis

In order to assess the method working range, the following shall be available:

a) samples with known concentrations and sample blanks;

b) the instrument shall have been calibrated..

For the analysis of impurities in H_2, the higher value of the working range shall be at least equal to 2 times the threshold value. The lower value of the working range (either LOQ or lowest calibration standard) shall respect the Formula (5).

The quantification of impurities in H_2 samples should be done by direct comparison with calibration mixtures by use of methods described in, e.g. ISO 12963[6] (single point, bracketing), or ISO 6143[7] (multiple points). An alternative protocol using standard addition method is also described in ISO 19229[8].

6.2.4 Trueness

6.2.4.1 Definition and calculation

Measurement 'trueness' is an expression of how close the mean of a large number of results (produced by the method) is to a reference value. We can make a practical assessment of the trueness by repeated

measurements of a reference material. This assessment is normally expressed quantitatively in terms of 'bias', see references [9][10].

A practical determination of the trueness is based on the measurement of bias and relies on comparison of the mean of the results (x_{mean}) obtained from the method with a suitable reference value (x_{ref}). One of the three following approaches shall be used:

a) analysis of certified reference materials

To determine the bias using a Certified Reference Material (CRM), the mean (x_{mean}) and standard deviation of a series of replicate measurements are determined and the results compared with the assigned property value of the CRM(x_{CRM}). In the purpose of this standard, the ideal CRM is a certified gas mixture in hydrogen balance gas.

The bias, b, can be expressed in absolute terms according Formula (6):

$$b = x_{mean} - x_{CRM} \tag{6}$$

or relative in per cent according Formula (7):

$$b(\%) = \left(\left(x_{mean} - x_{CRM} \right) / x_{CRM} \right) \times 100 \tag{7}$$

b) recovery experiments using spiked samples

In the absence of suitable CRMs, recovery studies using spiking and unspiking samples are used to give an indication of the likely level of bias. The spike addition to the sample shall be done using accurate protocol. The analytical result of the spiked sample is compared to the expected spike concentration.

In that case, the bias can be expressed as relative spike recovery according Formula (8):

$$R'(\%) = \left(\left(x'_{mean} - x'_{blank} \right) / x_{spike} \right) \times 100 \tag{8}$$

where x'_{mean} is the mean value of the spiked sample, x'_{blank} is the mean value of the unspiked sample and x_{spike} is the added concentration to the sample.

c) participation to interlaboratory comparison

It is also possible to assess bias by comparing results from the method used by the laboratory (x_{mean}) to the reference value access during a proficiency test($x_{refproficiency}$). The biais of the laboratory will be measured by the Formula (9):

$$b = x_{mean} - x_{refproficiency} \tag{9}$$

6.2.4.2 Fit for purpose for H_2 analysis

In order to assess the fit for purpose of the analytical method, the bias of the method shall be determined at concentrations close to the threshold value using one of the above three approaches.

This bias shall be small enough to have a relative combined uncertainty below 10 % of the concentration. Exception could be accepted for total sulphur and formaldehyde measurement. In these cases, higher relative uncertainties could be accepted but relative uncertainty should not be higher than 50 %.

6.2.5 Precision

6.2.5.1 Definition and calculation

Precision (measurement precision) is a measure of how close results are to one another[3],[5]. It is usually expressed by the standard deviation (or relative standard deviation), calculated from results obtained by carrying out replicate measurements on a suitable material under specified conditions.

'Measurement repeatability' and 'measurement reproducibility' represent the two extreme measures of precision which can be obtained.

Repeatability, expected to give the smallest variation in results, is a measure of the variability in results when a measurement is performed by a single analyst using the same equipment over a short timescale.

Reproducibility, expected to give the largest variation in results, is a measure of the variability in results between laboratories.

Between these two extremes, 'intermediate (measurement) precision' gives an estimate of the variation in results when measurements are made in a single laboratory but under conditions that are more variable than repeatability conditions. The exact conditions used should be stated in each case. The aim is to obtain a precision estimate that reflects all sources of variation that will occur in a single laboratory under routine conditions (different analysts, extended timescale, different pieces of equipment, etc.).

Precision is generally dependent on analyte concentration, and so should be determined at a number of concentrations across the range of interest. For the purpose of this standard, the precision could be determined for samples with concentrations at the limits of the measuring interval. If relevant, the relationship between precision and analyte concentration should be established. In cases where the measured concentration is well above the detection limit, the precision is often found to be proportional to analyte concentration. In such cases it may be more appropriate to express precision as a relative standard deviation since this is approximately constant over the range of interest.

Evaluation of precision requires sufficient replicate measurements to be made on suitable materials. The materials should be representative of test samples in terms of matrix and analyte concentration, homogeneity and stability, but do not need to be Certified Reference Materials. The minimum number of replicates specified varies with different protocols, but is typically between 6 and 15.

6.2.5.2 Fit for purpose

In order to assess the fit for purpose of the analytical method, the precision of the method shall be determined at least at concentrations close to the threshold value and the precision for this concentration shall be small enough to have a relative combined uncertainty below 10 % of the concentration.

Exception could be accepted for total sulphur and formaldehyde measurement. In these cases, higher relative uncertainties could be accepted but relative uncertainty should not be higher than 50 %.

6.2.6 Measurement uncertainty

6.2.6.1 Definition and calculation

The uncertainty of an analytical procedure evaluates its ability to produce accurate results. Thus, the uncertainty estimation is fundamental to assess the validity of a method. This uncertainty is mainly due to trueness (bias) and precision plus the impact of calibration or external parameters like temperature or pressure.

A full discussion of (measurement) uncertainty is beyond the scope of this standard but detailed information can be found elsewhere[6,7]. Uncertainty is associated with a measurement result which expresses the range of values that can reasonably be attributed to the quantity being measured.

An uncertainty estimate should take account of all recognised effects operating on the result. The uncertainties associated with each effect are combined according to well-established procedures[12].

Several approaches to obtaining an uncertainty estimate for the results from chemical measurements are described[13,15-17]. These take into account:

— the overall, long-term precision of the method (i.e. the intermediate precision or reproducibility);

— bias and its uncertainty, including the statistical uncertainty involved in the bias measurements, and the uncertainty in the reference value, see references [18]-[22];

— equipment calibration. Uncertainties associated with calibration of analytical equipment;

— any significant effects operating in addition to the above. For example, temperature, pressure or time ranges permitted by the method may not be fully exercised in validation studies, and their effect may need to be added. Such effects can be usefully quantified by ruggedness studies or related studies which establish the size of a given effect on the result.

6.2.6.2 Fit for purpose

In order to assess the fitness for purpose of the analytical method, mixtures close to the threshold value should be prepared by spiked addition to pure hydrogen. The uncertainty should be determined for each impurity. The spiked samples should be measured using the developed analytical method. The relative combined uncertainty for that concentration should be below 10 % of the concentration[23]-[24].

Exception could be accepted for total sulphur and formaldehyde measurement. In these cases, higher relative uncertainties could be accepted but relative uncertainty should not be higher than 50 %.

6.2.7 Robustness

6.2.7.1 Definition and calculation

In any method there will be certain stages which, if not carried out sufficiently carefully, will have a significant effect on method performance and may even result in the method not working at all. These stages should be identified, usually as part of method development, and if possible, their influence on method performance evaluated using a 'ruggedness test' ('robustness test').

A 'ruggedness test' involves making deliberate changes to the method, and investigating the subsequent effect on performance. It is then possible to identify the variables in the method which have the most significant effect and ensure that, when using the method, they are closely controlled.

6.2.7.2 Fit for purpose

This is no specific requirement for the robustness but the critical parameters should be investigated to ensure that, when using the method, they are closely controlled.

6.3 Validation report

A validation report describing all the tests done for the evaluation of all the characteristics of the analytical methods should be done. This report should be presented upon request.

A simple template for a validation report could, e.g. consist of the following sections[25]:

— **Title**: This section should identify the method and when and who is performing the work. Brief information about the method scope and a short description of the method should be given, as well as details of the status of the method (e.g. an international standard, a method developed in-house etc.), the analyte, measurement unit, types of sample and the intended use. Sampling can be part of the measurement procedure and shall, in those cases, be validated. Even if these steps are performed elsewhere, it is useful to include information about them in the validation plan/report.

— **Planning**: This section should outline the purpose, e.g. full validation of a new method, verification of performance of a standardized method, extension to method scope, etc. The extent of the validation work should be indicated, i.e. the performance characteristics which will be investigated and any associated requirements.

— **Performance characteristics**: This section should give a brief explanation of the performance characteristic, repeat any specific requirements, outline the experiments which will be done and how the results are to be evaluated. Results and conclusions from the experiments should be stated. Separate sections are used for each performance characteristic.

— **Summary**: The last section summaries the validation work and the results. Implications concerning routine use, and internal and external quality control, can be given. Most importantly, a concluding statement as to whether the method is fit for purpose shall be given.

6.4 Quality Control of the analytical method

Method validation gives an idea of a method's capabilities and limitations which may be experienced in routine use while the method is in control. Specific controls shall be applied to the method to verify that it remains in control, i.e. is performing in the way expected.

During the validation stage the method was largely applied to samples of known content. Once the method is in routine use it is used for samples of unknown content. Suitable internal QC shall be applied by continuing to measure stable test samples, thus allowing the analyst to decide whether the variety of answers obtained truly reflects the diversity of samples analysed or whether unexpected and unwanted changes are occurring in the method performance. In practice these known samples should be measured with every batch of samples as part of the quality control process.

7 Analytical techniques

The table below lists analytical methods that can be suitable for measurement of impurities in hydrogen as required by ISO 14687 (note that these methods shall be fully validated according to the previous protocol by each laboratory before initial use).

This table reflects the existing state of the art analytical techniques but others can be applied if fully validated according to the previous protocol.

Table 2 — Analytical methods suitable for measurement of impurities in hydrogen

Impurity	ISO 14687-2 limit ($\mu mol\ mol^{-1}$)	Analytical technique	Considerations	Reference[20]
Water	5	Chilled mirror hygrometer (Dew point meter)	A	*Murugan and Brown (2014)*
		Quartz crystal microbalance	A	*Murugan and Brown (2014)*
		CRDS	A	*NPL Report* AS 64
		Capacitance	A	JIS K0512
		Continuous wave CRDS	A	ASTM D7941
		GC-MS		*NPL Report* AS 64
		GC-MS with jet pulse injection		ASTM D7649
		FTIR	A	ASTM D7653 JIS K0512

Table 2 *(continued)*

Impurity	ISO 14687-2 limit (μmol mol^{-1})	Analytical technique	Considerations	Reference[20]
Total hydrocarbon content (THC)	2	GC-FID	D	ASTM D7675 JIS B 7956
		Methaniser-GC-FID		*NPL Report* AS 64
		GC-MS (with pre-concentrator)	A,B	ASTM WK34574
		FTIR	A	ASTM D7653
Oxygen	5	Electrochemical sensor	A	ASTM D7607
		GC-MS with jet pulse injection		ASTM D7649
		GC-TCD		*NPL Report* AS 64
		GC-PDHID		*NPL Report* AS 64
		Continuous wave CRDS	A	ASTM D7941
Helium	300	GC-TCD	E	*NPL Report* AS 64
Nitrogen	100	GC-TCD		*NPL Report* AS 64 JIS K 0512
		GC-PDHID		*NPL Report* AS 64
		GC-MS with jet pulse injection		ASTM D7649
Argon	100	GC-TCD		*NPL Report* AS 64
		GC-PDHID		*NPL Report* AS 64
		GC-MS with jet pulse injection		ASTM D7649
Carbon dioxide	2	Methaniser-GC-FID		*NPL Report* AS 64 JIS K 0114
		GC-PDHID		*NPL Report* AS 64
		GC-MS with jet pulse injection		ASTM D7649
		FTIR	A	ASTM D7653
		Continuous wave CRDS	A	ASTM D7941
Carbon monoxide	0.2	GC-PDHID		*NPL Report* AS 64
		Methaniser-GC-FID		*NPL Report* AS 64 JIS K 0114
		FTIR	A	ASTM D7653
		Continuous wave CRDS	A	ASTM D7941
Total sulphur compounds	0.004	GC-SCD (with pre-concentrator)	A,B	ASTM D7652
		GC-FPD (with pre-concentrator)	A	JIS K 0512
		GC-SCD (without pre-concentrator)	D	*Murugan and Brown (2014)*
Formaldehyde	0.01	GC-MS (with pre-concentrator)	A,B	ASTM D7892
		GC-MS (without pre-concentrator)		*NPL Report* AS 64
		Continuous wave CRDS	A	ASTM D7941
		HPLC (with DNPH cartridge)	A, B	JIS K0303
		FTIR	A	ASTM D7653
Formic acid	0.2	FTIR	A	ASTM D7653
		IC with impinger sampling device	A,B	JIS K0127

Table 2 *(continued)*

Impurity	ISO 14687-2 limit (µmol mol^{-1})	Analytical technique	Considerations	Reference[20]
Ammonia	0.1	GC-MS		*NPL Report* AS 64
		FTIR	A	ASTM D7653
		IC	A,B	ASTM D7550
		IC with impinger sampling device	A,B	JIS K0127
		Continuous wave CRDS	A	ASTM D7941
Halogenated compounds	0.05	IC with impinger sampling device	A,B	JIS K0127
		GC-MS (with pre-concentrator)	A,B,F	ASTM D7892

Considerations:

A: Analysis may require a volume of gas greater than 0.5 liter

B: Analytes may be lost during enrichment or bubbling step

C: Stabilisation time (to reach steady state) may be high

D: A non-retaining column shall be used

E: Helium carrier gas cannot be used

F: Only organic compounds are detected

8 Sampling

8.1 Sampling strategy

Established sampling strategies for hydrogen fuel quality control are documented by ISO 19880-1, Annex I. Samples should be collected at the HRS nozzle and be representative of the duration of the refuelling protocol.

The purging requirements for the various sampling devices depend on parameters like internal volume, materials and passivation thereof. Purging of the device with UHP hydrogen in order to avoid cross contamination of samples should be performed. The ratio of the sampling device internal volume to the sample volume to be collected give indication of the minimum purging requirement of the sampling device.

In the event of simultaneous sampling of gases and particulates, gases should be sampled upstream any particulate filter in order to avoid condensation and other losses of gas species onto filter.

Care should be taken as to avoid pressurization of devices containing air with hydrogen.

8.2 Sampling vessels

Vessels with a passivated internal surface are strongly recommended to avoid impurity losses and contaminant crossover between samples.

Sample vessel purging requirements may vary with sampling strategy and vessel type. In the case of open-ended vessels, a sufficient amount of UHP hydrogen shall be purged through the vessel in order to avoid cross-contamination.

Vessel preparation before sampling is normally conducted by evacuation to a level of 0,1 kPa or lower. Dependent on sampling history and impurity exposure levels, a repeated sequence of evacuation and pressurization with UHP hydrogen is recommended.

Transfer or sample from original vessel should be avoided as to minimize risk of impurity losses as well as contamination. In any case, sample transfer shall be documented with relevant data like vessel type and time before and after transfer.

The sampling vessel shall respect the local regulation for transportable pressure equipment (e.g. the European one, see reference [27]).

8.3 Samples

For analysis the requirements for sample volume and pressure shall be known and sufficient material collected.

Sample stability in vessel cannot be assumed, and minimal time between sampling and analysis is strongly recommended.

Calculation of air constituent ratios should be conducted from the analytical results in order to ensure that the sample has not been contaminated by air.

9 Analytical report

The results of each sample analysis carried out by the laboratory shall be reported accurately, clearly, unambiguously and objectively, and in accordance with any specific instructions in the test or calibration methods.

The results shall be reported, usually in a test report and shall include all the information requested by the customer and necessary for the interpretation of the analytical results and all information required by the method used.

In the case of analysis performed for internal customers, or in the case of a written agreement with the customer, the results may be reported in a simplified way.

Any information listed in the following sections which is not reported to the customer shall be readily available in the laboratory which carried out the sample analysis.

Each analytical report shall include at least the following information, unless the laboratory has valid reasons for not doing so:

a) a title (e.g. “Analytical Report”);

b) the name and address of the laboratory, and the location where the analysis were carried out, if different from the address of the laboratory;

c) unique identification of the analytical report (such as the serial number), and on each page an identification in order to ensure that the page is recognized as a part of the test report and a clear identification of the end of the report;

d) the name and address of the customer;

e) identification of the method used and information if the method is validated (i.e. internal validation or reference to a standardised method);

f) a description and unambiguous identification of the sample analysed;

g) the date of sampling (if the laboratory was in charge of the sampling), the date of receipt of the sample in the laboratory (where this is critical to the validity of the results), and the date(s) of performance of the analysis;

h) the analytical results with the units of measurement;

i) a statement on the estimated uncertainty of measurement (with the coverage factor used);

j) the name(s), function(s) and signature(s) or equivalent identification of person(s) authorizing the analytical report.

Sample analytical reports shall also, where necessary for the interpretation of the test results or where the sampling was performed by the analytical laboratory, include the following:

a) deviations from, additions to, or exclusions from the validated method, and information on specific test conditions, such as environmental conditions;

b) the reference to the standard gas mixtures used for the analysis;

c) unambiguous identification of the hydrogen sampled (including the name of the manufacturer, the location);

d) If the sampling is performed by the laboratory, the location of sampling, including any diagrams, sketches or photographs;

e) details of any environmental conditions during sampling that may affect the interpretation of the test results;

f) details of any environmental conditions during sampling that may affect the interpretation of the test results;

g) any standard or other specification for the sampling method or procedure, and deviations, additions to or exclusions from the specification concerned.

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