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

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Foreword

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This document was prepared by Technical Committee ISO/TC 158, *Gas analysis* in collaboration with Technical Committee ISO/TC 197, *Hydrogen technologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The hydrogen supply infrastructure for fuel cell electric vehicles (FCVs) requires specifications and an operational protocol for maintaining the quality of the hydrogen used to fuel the vehicles. To fulfil these requirements, several documents have been written: ISO 14687 which sets forth the quality specifications of hydrogen, and ISO 19880-8 which specifies 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 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.

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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 (H_2) at hydrogen distribution bases and hydrogen fuelling stations for road vehicles using proton exchange membrane (PEM) fuel cells. It also gives recommendations on the calculation of an uncertainty budget for the amount fraction.

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

This document gives a list of suitable analytical techniques used to measure each impurity in hydrogen, according to the specification of hydrogen grade D defined by ISO 14687:—[1].

Moreover, recommendations for keeping the integrity of the sample are also given in order to ensure the quality of the measurement. It also includes the requirements for reporting the analytical results.

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 quality — Product specification*

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 https://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

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1) Under preparation. Stage at the time of publication: ISO/DIS 14687:2018.

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 a limit of detection (LOD) or limit of quantification (LOQ)
s_r	repeatability standard deviation
s_R	reproducibility standard deviation
u	standard uncertainty
x_{CRM}	certified property value of a certified reference material
x_{LOD}	value of the limit of detection
x_{LOQ}	value of the limit of quantification
$x_{threshold}$	value of the specification for each impurity listed in ISO 14687:— grade D
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
$x_{refproficiency}$	reference value assigned during a proficiency test
x_{spike}	added concentration in a recovery experiment

5 Quality 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 at the dispenser nozzle applicable to the hydrogen fuel for PEM fuel cells in road vehicles shall meet the requirements of grade D of ISO 14687:—.

6 Requirements for analytical method validation and fit for purpose

6.1 General

Method validation of fit for 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 as described in Eurachem guide [2]. Using the information produced during 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 shall not be used for the analysis of impurities in H_2; another method shall be used.

A laboratory may adopt a validated procedure which 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 of these cases, basic validation work has already been carried out but the laboratory shall confirm its ability to apply the method. This 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 Characteristics for analytical methods

6.2.1 List of main characteristics

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	Clause/Subclause
Selectivity	6.2.2
Limit of detection (LOD) and limit of quantification (LOQ)	6.2.3
Working range	6.2.4
Trueness bias, recovery	6.2.5
Precision repeatability, intermediate precision and reproducibility	6.2.6
Measurement uncertainty	6.2.7
Ruggedness (robustness)	6.2.8

6.2.2 Selectivity

6.2.2.1 Definition and estimation

Analytical selectivity relates to "the extent to which the method can be used to determine particular analytes in mixtures or matrices without interferences from other components of similar behaviour"[3].

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).

6.2.2.2 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 also be studied.

6.2.3 Limit of detection and limit of quantification

6.2.3.1 Definition and calculation

It is necessary to distinguish between the instrument detection limit and the method detection limit (x_{LOD}). 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, for example, a chromatogram.

To obtain the method detection limit x_{LOD}, the calculation shall be based on the analysis of samples according to 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 (x_{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 x_{LOQ} is typically 4 to 20 times the standard deviation of a low level sample or blank measurement[2].

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

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

b)   test samples with concentrations of analyte close to expected x_{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 x_{LOD} are required. These can be prepared by spiking a blank sample.

The standard deviation s_0 is normally obtained under repeatable conditions. It is important that this standard deviation is 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 at least 6 to give a representative value; 10 replicates are often recommended in validation protocols. The standard deviation s_0 is obtained by the following Formula (1).

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

where

x_i is the measurement i;

x_{mean} is the average value;

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

In many measurement procedures, the mean of n replicates is reported in the 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 the routine use following Formula (2):

$$s_0' = \frac{s_0}{\sqrt{n}} \tag{2}$$

Both x_{LOD} and x_{LOQ} are normally calculated by multiplying the standard deviation s_0' by a suitable factor[4]. The x_{LOD} shall be calculated using Formula (3):

$$x_{LOD} = 3 \times s_0' \tag{3}$$

x_{LOQ} is calculated using Formula (4):

$$x_{LOQ} = k_Q \times s_0' \tag{4}$$

This will be sufficient if an estimate of the limit of detection and limit of quantification is required simply to demonstrate that the concentrations of samples will be well above these values. Where laboratory samples are expected to contain low concentrations of the analyte, both limit of detection and limit of quantification should be monitored on a regular basis. This could be the case for the impurities at the lowest quality specifications where the limit of quantification could be close to the specification value (for example sulphur compounds analysis).

6.2.3.2 Fit for purpose for H_2 analysis

The calculation of x_{LOQ} shall be done according to Formula (4) with the following rules:

— k_Q = 10 for specification values equal or above 1 μmol/mol

— k_Q = 5 for specification values less than 1 μmol/mol and above 10 nmol/mol

— k_Q = 3 for specification values equal or less than 10 nmol/mol, meaning that the limit of quantification is equal to the limit of detection

The limit of quantification of the analytical method shall be below the specification value in order to be able to quantify the impurity in the sample. The criterion for acceptance shall meet the conditions specified in Formula (5):

$$x_{LOQ} + u_{LOQ} < x_{threshold} \tag{5}$$

where u_{LOQ} is the uncertainty at the x_{LOQ} value.

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

6.2.4 Working range

6.2.4.1 Definition and calculation

The "working range" is the interval over which the method provides results with an acceptable uncertainty[2].

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

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