Metrology for sustainable hydrogen energy applications

JRP EMPIR 15NRM03
HYDROGEN

WP2: Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.2: Methods development

A2.2.4: Instrument specifications for the development of multi-component analysers using input from A1.3.1

This work has been carried out by

Karine Arrhenius, RISE

Thomas Bacquart, NPL

Frédérique Haloua, LNE

Stefan Persijn, VSL

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Summary

For routine laboratory/analysis, performing the whole set of analysis required by ISO14687-2 [1] is currently extremely challenging. Traceability of the measurements, trueness and detection limits are some of the critical point. As a large number of components need to be quantified, it is not possible to analyse all the components using a single method; on the contrary, many methods are required. The latest developed multi-component instruments have the potential to meet the required detection limits according to ISO14687-2. These instruments need to be designed based on the client´s specifications (number of compounds to be analysed simultaneously, the analytical measuring range…). However, it is not probable that all impurities listed in ISO14687-2 will be present in one sample; on the contrary depending on the method of production, only some impurities may be present in the hydrogen. Moreover, all impurities listed in ISO 14687-2 won´t have the same impact on fuel cell systems. By combining the probability of presence and the impact on the fuel cell system, a shorter list of impurities are highlighted. This is the aim of the task 1.3 (Risk Assessment) of this project. In this report, we have listed instrument specifications for the further development of multi-components analysers using the input of the risk assessment performed in task 1.3.

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1   Introduction

Performing the 13 analyses (gaseous compounds) required in ISO 14687-2 [1] to assess hydrogen quality require multiple analysis techniques mostly due to challenging detection limits to reach. Therefore some instrument manufacturers now offer the possibility to use multi-component analyzers in order to reduce the number of analyses totally required. The latest developed multi-component analyzers have the potential to meet the required detection limits but need to be designed based on the clients´specifications. Clients may base the specifications on different factors: taking into other instruments already available at the laboratory or focusing on impurities based on probability of presence or/and impact of impurities of fuel cell system.

Once impurities have been selected, the clients will need to decide on requirements for characteristic performances, costs and possibly other specific requirements (response time, volume the gas needed, possibility to work with different gas matrices).

In this report, we discuss risk assessment (including probability of finding impurities depending on the production method and impact and fuel cell system) as well as specifications related to the characteristic performance. Information are gathered from other activities performed in this project as well as information given in the ISO 14687-2 standard and the upcoming ISO 21087 standard [2].

2   Risk assessment

2.1   Probability of the presence of impurities depending on production method

The production risk assessment performed in task 1.1 [3] of this project (assessment of probability of impurities existing in real samples of hydrogen) is presented in table 1 for steam methane reforming with PSA, Chlor-alkali process and PEM water electrolysis process together with similar information for alkaline electrolyser obtained in standard ISO19880-8 [4].

Table 1: Probability of presence of impurities based on production method

Probability of impurity presence	Steam methane reforming with PSA	Chlor-alkali process (membrane cell process)	PEM water electrolysis process with TSA	Alkaline electrolyser*
Frequent	CO	O_2	None identified	None identified
Possible	N_2	None identified	None identified	N2
Rare	CH_4, H_2O and Ar	N_2 and H_2O	N_2, O_2 and H_2O	O2, H2O
Very rare	CH_2O	CO_2	CO_2	Ar
Unlikely	He, CO, O_2, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds	CO_2, CO, CH_4, Sulphur compounds, NH_3, hydrocarbons compounds, halogenated compounds, CH_2O, CH_2O_2, He

*from ISO19880-8

2.2   Combined risk assessment

The impact of impurities on fuel cell systems must also be considered in order to complete the risk assessment. This work done in task 1.3 will result in prioritisation matrices for different production methods. The matrices are obtained by combining the risk of occurrence (obtained from experts from level 1 to 5 and analytical campaign) with the final impact (taking into account both reversible and irreversible impact). The importance of the impurity is then the product of the risk of occurrence and the final impact. At the time this report was written, the matrices were not available.

3   Simultaneous analysis of several compounds

The latest developed multi-analyzers often rely on gas cells as nearly every small gas-phase molecule (e.g. CO_2, H_2O, H_2S, NH_3) has a unique near-infrared absorption spectrum. Every sensor has some cross-sensitivity, where the sensor responds to other gases. It is therefore important to be aware of potentially cross-sensitive compounds. Exposing a sensor to a gas that is not the target gas can cause an undesirable response, either positive or negative. Many of these instruments can be used online and offline. Other classical analytical methods allow the simultaneous analysis of several impurities such as gas chromatography (with for example a mass spectrometer for detection) and FTIR.

4   Specifications related to method performances

The validation of an analytical method allows assessing the method suitability for a particular purpose. The validation of the method gathers experimental work done to demonstrate that the method works in the end-user´s laboratory. Several parameters are considered as performance characteristics commonly evaluated during method validation: selectivity, limit of detection (LOD) and limit of quantification (LOQ), working range, trueness (bias, recovery), precision (repeatability, intermediate precision and reproducibility) and robustness. The evaluation of most of the parameters allows then to calculate the measurement uncertainty associated with a method for a component to be measured in a specified matrix. Several documents are available to guide a laboratory through a method validation including the Eurachem guide "The Fitness for purpose of analytical methods" [5]. In the case of validation data produced by an instrument manufacturer, it is recommended that the validation data are also evaluated by the end-user. The description of the performance characteristics below addresses the performance of the instrument (inclusive the sampling line) and not the whole method. ISO/CD 21087:2017 [2] currently under development provides valuable information regarding analytical methods and procedure in order to comply with hydrogen quality required by ISO14687.

4.1   Detection limit/quantification limit

Different definitions exist for the detection limit.

The detection limit (LOD) of an instrument is the lowest amount of analyte in a sample presented directly to the instrument (i.e. omitting any sample preparation) which can be detected but not necessarily quantitated as an exact value [2].

There is difference [6] for **Instrument Detection Limit** (IDL)—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal and **Method Detection Limit** (MDL)

For IUPAC [7]: The limit of detection, expressed as the concentration, c_L, or the quantity, q_L, is derived from the smallest measure, x_L, that can be detected with reasonable certainty for a given analytical procedure. The value of x_L is given by the equation

$$x_L = \bar{x}_{bi} + k\, s_{bi}$$

where $\bar{x}_{bi}$ is the mean of the blank measures, s_{bi} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired.

In JCGM 200:2012 (VIM) [8]: measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence NOTE 1 IUPAC recommends default values for α and β equal to 0.05.

The quantification limit also called determination limit (LOQ) of an instrument is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy [2].

The quantification limit shall be less than or equal to the limits (also called threshold values) presented stated in the standard ISO14687-2. A criterion for acceptation is presented in ISO/CD 21087:2017 [2] as:

LOQ + u_{LOQ} < limits in ISO14687-2

For example, if the uLOQ is 20% (acceptable for most compounds) or 50% (formaldehyde or hydrogen sulphide) of the LOQ, the quantification limits for the components to be analyzed in ISO14687-2 will be the ones listed in table 2.

Generally, instrument´s detection limit and quantification limits can be calculated using the method of the ratio of the signal to the noise (S/N ratio) or the method of the standard deviation. The determination of the S/N ratio is performed by comparing measured signals from sample with known low concentrations of analyte with those of blank samples and by establishing the minimum concentration at which the analyte can be reliably quantified. A typical S/N for LOD is 3:1 and for LOQ 10:1. The method used to assess the LOD and the LOQ should be specified clearly by the instrument manufacturer so the end-user can assess/confirm the provided data.

Components	Instrument´s required LOQ (u_{LOQ} = 50% of LOQ)	Instrument´s required LOQ (u_{LOQ} = 20% of LOQ)
Water	3	4
Total hydrocarbons (CH4 basis)	1	1.6
Oxygen	3	4
Helium	150	240
Total Nitrogen and argon	50	80
Carbon dioxide	1	1.6
Carbon monoxide	0.1	0.16
Total Sulphur compounds (H2S, COS, CS2 and mercaptans as a basis)	0.002	0.0032
Formaldehyde	0.005	0.008
Formic acid	0.1	1.6
Ammonia	0,05	0,08
Total halogenated compounds (Hbr, HCl,	0.03	0,04

Cl2 or organic halides)		

<p align="center">* calculated with $u_{LOQ} = 50\%$ of LOQ</p>

<p align="center">***Table 2: Required LOQ of instruments for the components listed in ISO14687-2***</p>

A detailed procedure to assess the detection limit is proposed by the U.S. E.P.A in the document 40CFR Part 136 [6]. By convention, the reliability of an analytical instrument is considered as three times the limit of quantification.

4.2   Working range

The working range is the interval over which the instrument provides results with an acceptable uncertainty [9]. The lowest value is the LOQ. The highest value shall be at least equal to 2 times the limits proposed in ISO14687-2, see table 3.

Components	Highest value of working range
Water	10
Total hydrocarbons (CH4 basis)	4
Oxygen	10
Helium	600
Total Nitrogen and argon	200
Carbon dioxide	4
Carbon monoxide	0.4
Total Sulphur compounds (H2S, COS, CS2 and mercaptans as a basis)	0.008
Formaldehyde	0.02
Formic acid	0.4
Ammonia	0.2
Total halogenated compounds (Hbr, HCl, Cl2 or organic halides)	0.1

<p align="center">***Table 3: Required highest value of working range of instruments for the components listed in ISO14687-2***</p>

Another approach has been proposed in the MetroHyVe project (EMPIR 16ENG01) by partners: using 10 or 20 times the threshold (limit values in ISO14687). The potential working ranges are presented in table 4.

	ISO14687	Potential working range	
Parameter	Threshold	10 * threshold	20 * threshold
CO	0.2	0.02 - 2	0.01 – 4
Halogen.	0.05	0.005 – 0.5	0.0025 – 1.0
Formic acid	0.2	0.02 - 2	0.01 – 4
CH2O	0.01	0.001 – 0.1	0,0005 – 0.2
Ammonia	0.1	0.01 - 1	0.005 - 2

Total sulphur	0.004	0.0004 – 0.04	0.0002 – 0.08
H_2O	5	0.5 - 50	0.25 - 100
Tot. hydrocarb.	2	0.2 - 20	0.1 - 40
CO_2	2	0.2 - 20	0.1 - 40
CH_4	100	10 - 1000	5 - 2000
N_2	300	30 - 3000	15 - 6000
Ar	300	30 - 3000	15 - 6000
He	300	30 - 3000	15 - 6000

4.3   Selectivity

The selectivity [4] refers to the extent to which the instrument can be used to determine particular analytes in mixtures or matrices without interferences from other components.

The selectivity of an instrument is acceptable if the presence of suspected interferents do not inhibit detection or quantification of the targeted analytes [2].

The selectivity should be verified for all contaminants at ISO14687-2 threshold and in extrem cases as followed:
- H2O up to 1000 ppm (failure of water purification from electrolyser system)
- N2 up to 4000 ppm issue with purging
- O2 up to 100 ppm issue with air leak
- Ar up to 400 ppm problem of purging
- CO up to 100 ppm
- Light hydrocarbons up to 100 ppm (methane, ethane, propane, butane)
- Ammonia up to 100 ppm (feedstock or Liquid Organic Hydrogen Carrier (LOHC)).

4.4   Precision

Precision is a measure of how close results are to one another [5].

In JCGM 200:2012 (VIM) [8]:
Closeness of agreement between **indications** or **measured quantity values** obtained by replicate **measurements** on the same or similar objects under specified conditions.

Definition in the VIM followed by four notes that are:
NOTE 1 Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.
NOTE 2 The 'specified conditions' can be, for example **repeatability conditions of measurement**, **intermediate precision conditions of measurement**, or **reproducibility conditions of measurement** (see ISO 5725-1:1994).
NOTE 3 Measurement precision is used to define **measurement repeatability**, **intermediate measurement precision**, and **measurement reproducibility**.
NOTE 4 Sometimes "measurement precision" is erroneously used to mean **measurement accuracy**.

It is usually expressed by statistical parameters which describe the spread of results (standard deviation or relative standard deviation):
- Repeatability: (give the smallest variation in results): measurements performed by a single analyst using the same equipment over a short timescale
- Intermediate precision (R_w): measurements performed by a single laboratory using for example different analysts, equipment and/or extended timescale
- Reproducibility (give the largest variation in results): measurements performed by different laboratories

The precision shall be determined at a number of concentrations across the working range, for example at the limits using a number of replicates typically between 6 and 15.
The precision is then used to calculate the expanded measurement uncertainty (U) of the method together with the trueness (bias) (and equipment calibration).
In ISO/CD21087, it is recommended that the method´s expanded uncertainty shall not exceed 20% rel. except for total sulfur and formaldehyde (50% rel.). This means that the combined uncertainty (uC) shall not exceed 10% rel. (25% for formaldehyde and total sulfur) if a coverage factor of 2 is used (typical value).

The combined uncertainty is often calculated as follow:

$$u_C = \sqrt{u(R_w)^2 + u(bias)^2}$$

If it is assumed that the trueness and the precision equally contribute to the combined uncertainty, the precision must then be 7% rel. max. (17-18% rel. for formaldehyde and total sulfur).

4.5   Trueness

The trueness is an expression of how close the mean of a number of results is to a reference value.
The reference value can be obtained using reference materials, spiked samples, from another method or from an interlaboratory comparison.
As explained in 4.4, If it is assumed that the trueness and the precision equally contribute to the combined uncertainty, the precision must then be 7% rel. max. (17-18% rel for formaldehyde and total sulfur).
JCGM 200:2012 (VIM) [8]:
Closeness of agreement between the average of an infinite number of replicate **measured quantity values** and a **reference quantity value**
NOTE 1 Measurement trueness is not a **quantity** and thus cannot be expressed numerically, but measures for closeness of agreement are given in ISO 5725.
NOTE 2 Measurement trueness is inversely related to **systematic measurement error**, but is not related to **random measurement error**.
NOTE 3 "Measurement accuracy" should not be used for 'measurement trueness'.

4.6   Measurement uncertainties

Expanded measurement uncertainty U is a parameter that characterizes the dispersion of the values that could reasonably be attributed to the results of a measurement. In other words, the result can be expected to lie with ± U units of the true value 95% of the time (if a coverage factor of 2 is used) if the same measurement were to be performed many times.

In ISO/CD21087, it is recommended that the method´s expanded uncertainty shall not exceed 20% rel. except for total sulfur and formaldehyde (50% rel.).

5 Costs

Several costs must be considered, they can be divided into capital costs which include the price of the instrument and the price for the installation of the instrument and operational costs which include the personnel, training and third party maintenance support costs, the maintenance and parts costs and the consumable costs. These costs are discussed in the sections below. The instruments providers should if possible give an estimation of these costs to the laboratory.

5.1 Capital costs

The capital costs include the price of the instrument inclusive all initial spare parts and the price for the installation of the instrument at the laboratory. Estimations of instrument prices (exclusive some parts) are given in activity A2.1.2 of this project. The laboratory will also need to prepare proper documentation as for example a preventive maintenance report. Support costs can be optimized if diagnostics can remotely be performed.

5.2 Operational costs

The operational costs include:

Personal, training and third party maintenance support costs

A significant cost factor is on-site personal costs. To optimize this cost, this is important to allocate personal with the proper degree of experience. Other costs include cost for preventive maintenance, support time from providers, unscheduled maintenance visits. Time for these moments should be estimated through discussion with the instrument provider.

Consumable parts costs

This category will vary markedly from instrument to instrument and should also carefully be estimated.

6 Other requirements

6.1 Response time

Sensors do not change output state immediately when an input parameter change occurs. Rather it will change to the new state over a period of time called the response time. The response time can be defined as the time required for an output to change from its previous state to a settled value within a tolerance interval of the correct new value.

The response time of a system depends on many factors: the sensor´s construction, the flow rate, the molecules being analysed etc.

Response time varies for each molecule depending on their characteristics. For instance, some molecules as H_2O and NH_3 are called "sticky" which means that they have an ability to adhere (stick) to itself (process called cohesion) and to surfaces due to bonds properties between atoms of the molecules. Molecules containing HO and NH bonds will tend to be sticky.

Passivation may be employed to prevent interaction of sticky molecules with interfaces inside of an instrument and thereby improve the response time. The passivation may need the presence of a highly polar functional group to prevent further binding of polar molecules.

6.2 Calibration using other matrices than hydrogen

In some cases, it can be an advantage to be able to work with other matrices than hydrogen. For example, it may be more convenient to obtain reference gas mixtures for instruments calibration or if the lab plans on using the instrument for other purposes.

6.3 Volume of gas available / needed

The volume, flow rate and the pressure needed are instrument dependent and can vary greatly depending on the technique used to measure one compound. Therefore, the sample volume and pressure must be known and sufficient material collected. Some information about volume needed for so called multi-components analysers will be given in report "Assessment of performances of multi-components analysers" as the result of activity A2.2.5 of this project.

The volume, flow rate and pressure available are dependent on where the sample is taken.
At the HRS: the pressure is 350 or 700 bar. In a cylinder of 1 liter, the volume of gas collected will be over 200L so instruments with flow rate of 1L/min are acceptable.
If the sample is taken from a buffer tank where the pressure is 20 -150 bar, instruments with high flow rate may be used but the volume of gases needs to be monitored. It is recommended to use flow rate lower than 500 ml/min with stabilisation time inferior to 60 min.
If the sample is taken at low pressure: 5 – 20 bar, the volume of gas will be from 5 to 20 liters, therefore the flow rate should be lower than 500 ml/min with stabilisation time inferior to 60 min. The system should be able to operate at 2 bar pressure or lower.

7 Summary of criteria and requirements

In table 5, the criteria and requirements discussed in the section above are summarized.

	Criteria	Requirements / Action / evidences
Simultaneous analysis of several compounds	List of compounds analysed	compare to priority lists
Specifications related to method performances		
Detection limit/quantification limit	LOQ + uLOQ (k=2) < ISO 14687	Verify detection limit with analysis of PRM
Working range	Preferably 10 * ISO 14687 (at least 2* ISO 14687)	Provide linearity plot
Selectivity (normal)	Interferences versus ISO 14687 composition	Literature or experiments If possible use PRM cocktail at ISO 14687 level
Selectivity (extrem)	Interference versus critical situation observed in real situation	Literature / Technical evidences
Precision	< 10 % rel at ISO level	use of PRM at ISO threshold
Trueness	< 10 % rel at ISO level	use of PRM at ISO threshold
Measurement uncertainties	< 20 % rel at ISO level < 50% CH2O and Sulphur	Provide calculation and equation including at least $uC = \sqrt{u(Rw)2+u(bias)2}$
Costs		
Capital costs	Equipment price	Check equipment price versus number of analysis and length life < 1 € / kg H2 produced

		Estimate operational cost and maintenance / year
Operational costs	Number of calibration / year	< 1 € / kg H2 produced (customer requirements)
Personal, training and third party maintenance support costs	Personal time requirement / year / maintenance	Cost estimation and target < < 1 € / kg H2 produced (customer requirements)
Other requirements		
Response time	Stabilisation time at ISO threshold	< 30 min for stabilisation
Calibration using other matrices than hydrogen	Which standards can be used	evidence of equivalence between PRM in hydrogen and other matrices
Volume of gas needed HRS Buffer low pressure	flow and time: 5 L/min and 30 min stabilisation 0.5L/min and 60 min stabilisation < 0.5L/min and 30 min stabilisation	Evidence of flow and stabilisation
Use at pressure	Effect of pressure on the system if offered	Demonstrate measurement with PRM at high pressure and no bias

*PRM: Primary reference materials

8   References

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[2] ISO/CD 21087:2017, Hydrogen fuel - Analytical methods - PEM fuel cell applications for road vehicles

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[6] "Guidelines establishing test procedures for the analysis of pollutants", CFR 40 Part 136, U.S. E.P.A., 2017

[7] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997).

[8] JCGM 200:2012, International vocabulary of metrology - Basic and general concepts and associated terms (VIM), 3rd edition, 2008

[9] Definition and procedure for the determination of the method detection limit, CFR40 appendix B to Part 126, U.S. E.P.A.