METROLOGY for HYDROGEN VEHICLES

Work Package 2 ‘Quality assurance’

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EMPIR EURAMET

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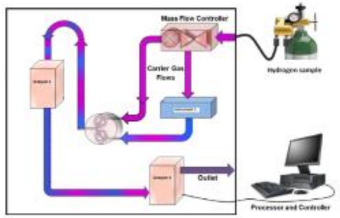
WP2 ‘Quality assurance’ Overview

Aim

To support hydrogen purity testing as specified in ISO 14687

- developing traceable offline gas analysis methods
- stable and accurate primary reference gas mixtures
- the metrological tools to enable the introduction of low cost gas analysers suitable for use by commercial gas analysis laboratories
- develop a robust method for accurately performing measurement of particulates



Develop and *validate* a *choice* of analytical methods and standards with *traceable reference values* to the existing and emerging hydrogen quality assurance laboratories.

Support the development of a European network of analytical laboratories capable of performing accurate hydrogen purity analysis as specified in ISO 14687

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WP2 Tasks

Task 2.1: **Validated Analytical Methods for Measuring Reactive Compounds – M1-M34**
(**VSL**, AP2E, AIR LIQUIDE, CEM, IFE, LINDE, NPL, SINTEF, RISE)

Task 2.2: **Validated Methods For Performing Traceable Measurement Of Particles – M1-M36**
(**NPL**, AIR LIQUIDE, ITM, NEN, SHELL, SINTEF)

Task 2.3: **Primary reference gas mixtures and dynamic reference standards for low level impurities in hydrogen – M1-M31**
(**CEM**, LINDE, NPL, VSL)

Task 2.4: **Optimisation of impurity enrichment devices – M1-M31**
(**NPL**, SINTEF)

Task 2.5: **A cost-efficient offline system for ISO 14687 purity analysis – M1-M34**
(**RISE**, AP2E, CEM, IFE, LINDE, NEN, NPL)

Task 2.6: **Interlaboratory comparison for ISO 14687 hydrogen measurements – M1-M36**
(**NPL**, AIR LIQUIDE, CEM, IFE, LINDE, SHELL, SINTEF, RISE, VSL)

Validated analytical methods for measuring reactive compounds

- **Objectives:**
  - Review, develop, validate and disseminate the best analytical methods available for offline testing of hydrogen purity according to ISO 14687

- Review existing methods for hydrogen purity (ISO 14687 scope);
- Assessment of ASTM standards and comparison to selected European validated method;
- Assessment of JIS standards and comparison to selected European validated method;
- Method validated following the guidelines of EURACHEM Guide and new document ISO/CD 21087 “Hydrogen fuel - Analytical methods - Proton exchange membrane (PEM) fuel cell applications for road vehicles”.

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Validated analytical methods for measuring reactive compounds

- *Halogenated compounds*: new method development and validation:
  - Selected halogenated compounds: Thermo desorption with gas chromatography and mass spectrometry (TD-GC-MS);
  - HCl (if possible Cl_2): Cavity ringdown spectroscopy (CRDS), Optical feedback cavity enhanced adsorption spectroscopy (OFCEAS), Ion chromatography (IC), pre-concentration with IC / electrolysis / ICP-MS.

Dichloromethane,
Tetrachloroethylene,
$C_4Cl_4F_6$,
Dichlorobenzene
Chloroform

- *NH_3, CH_2O_2, CH_2O:* new method development and validation:
  - GC based method;
  - Fourier transform infrared spectroscopy (FTIR);
  - Impinger (possibly solid phase extraction) with IC, capillary electrophoresis;
  - CH_2O_2, CH_2O: OFCEAS and CRDS;
  - NH_3, CH_2O_2: Filter with IC.

- *Sulphur compounds*: new method development and validation:
  - H_2S: OFCEAS;
  - H_2S and mercaptans: pre-concentration with IC / electrolysis / ICP-MS.

Carbonyl sulphide
Carbon disulphide
Tert-butyl mercaptan,
Tetrahydrothiophene,
Methylmercaptan

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Validated analytical methods for measuring reactive compounds

- Discussion:
  - Users of ASTM / JIS standards;
  - Important compounds with lack of analytical methods;
  - New analytical methods;
  - Method validation additional information (transfer of knowledge / process);
  - Relevance of the selected compounds for halogenated/sulphur compounds.

Validated methods for performing traceable measurement of particulates

- **Objectives:**
  - Good practice guide for handling and transporting filters for offline particulate sampling
  - Good practice guide on the best approach for traceable gravimetric weighing of particulate filters

- Validate a method based on ASTM D7651-10;
- Validate appropriate type of filter;
- Assessment of environmental contamination on the results;
- Comparison online analysis by Tapered elements oscillating microbalance (TEOM) and optical particulate monitor (OPC).

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Validated methods for performing traceable measurement of particulates

- Discussion

- Current status of particulate analysis:
  - Technical points:
    - Appropriate equipment: online / offline measurement;
    - Pressure (sampling at 350/700 bar or from sampling cylinder);
    - Transport of filter;
    - Preparation of filter.

  - Measurement issues:
    - Negative mass;
    - Presence of contaminant (liquid, oil);
    - Artefact, interference.

Primary reference gas mixtures and dynamic reference standards for low level impurities in hydrogen

- **Objectives:**
  - Development of static gas mixtures with traceable reference values and uncertainties
  - Development of dynamic gas standards with traceable reference values and uncertainties

- Review of passivation treatments available for gas cylinders
- Primary reference gas mixtures: H_2O, HCl, $C_4Cl_4F_6$ and one halogenated compounds
- Development of dynamic dilution system with dynamic reference value traceable to SI

  Critical orifices: sulphur compounds and ammonia

  Diffusion cells: CH_2O

Primary reference gas mixtures and dynamic reference standards for low level impurities in hydrogen

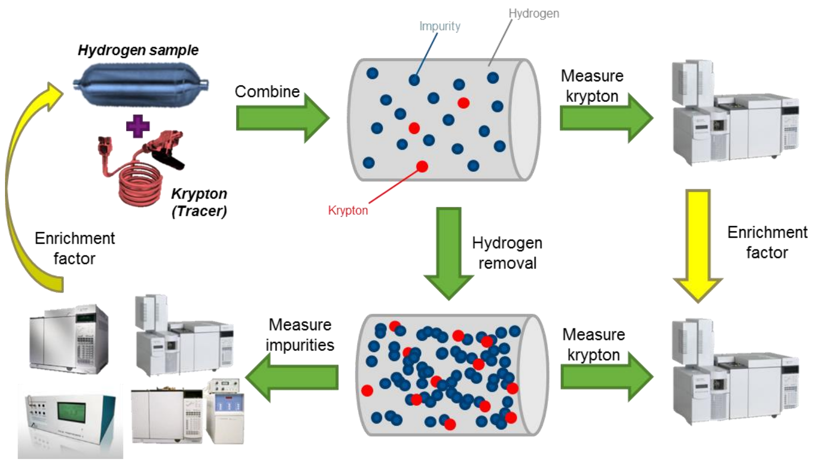
- Discussion:
  - Passivation of cylinder known (i.e. Sulfinert / Silconert2000 / spectraseal / Performax);

  - Type of dynamic dilution system used;
  - Calibration gas
  - Water vapour reference standards (amount fraction and stability)
  - Interest in PRM/PRGM for dilution system
    - Amount fraction: 100 times the ISO 14687 threshold
    - Volume of gas

Optimisation of impurity enrichment devices

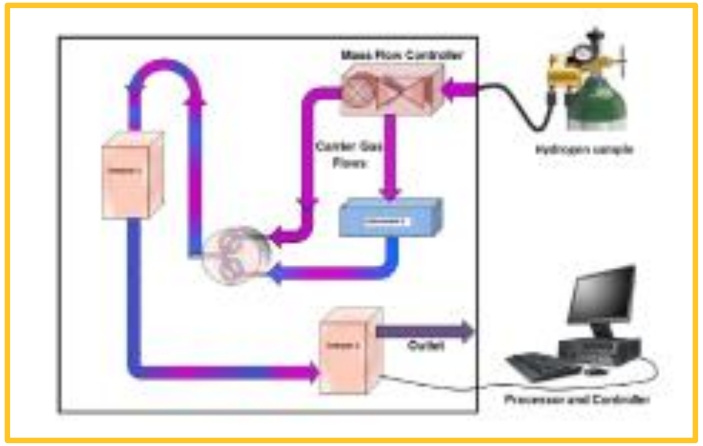
- **Objectives:**
  - Develop a hydrogen impurity enrichment device capable of concentrating low level impurities including hydrogen sulphide;
  - Define operating conditions and membrane to achieve an enrichment of factor 100
  - Demonstrate the technique capability on real sample with uncertainty budget

- Choice of membrane;
- Achievable amount fraction;
- Tracer: Krypton
- Instrument for final measurements: GC-MS



A cost efficient offline system for ISO 14687 purity analysis

- **Objectives:**
  - Design a system to perform offline measurement of all impurities in ISO 14687 by combining several analyser into one unique system
  - Reduce CAPEX by 30%, unbiased, relative expanded uncertainty below 20%
  - Guideline on how to implement the cost-efficient offline system with the good practice for calibrating the instruments



- Review existing analytical methods (including cost, accuracy), existing laboratory position and equipment
- Selection of the most suitable techniques;
- Design of the coupling system between instruments;
- Development, testing and validation using traceable standards

A cost efficient offline system for ISO 14687 purity analysis

- Discussion

  - Future users (end users, quality/process control)
  - Analytical instruments already available
  - Requirements:
    - Cost of the system: < 250k€ - < 350k€ - < 400k€
    - Parameters: full ISO 14687; reduced list (10 - 13 compounds); short list (4-7 compounds)
    - Delay to report results: 1 day – 1 week – 2 weeks
    - Uncertainty: < 5% - < 10% - < 25%
    - sample volume: < 10 litres - < 30 litres - < 100 litres

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Interlaboratory comparison for ISO 14687 hydrogen measurements

- **Objectives:**
  - Organise an interlaboratory comparison for more than 8 laboratories on CO, H_2S, O_2 and H_2O

- Design the interlaboratory comparison;
- Select the participants;
- Prepare, validate and ship the samples;
- Participants performed measurements;
- Data evaluation and interlaboratory comparison meeting and feedback;
- Report on the *results of the interlaboratory comparison for offline hydrogen purity analysis with conclusions on the participant agreement and recommendations for future improvements.*

A cost efficient offline system for ISO 14687 purity analysis

Compounds and proposed amount fraction:

	amount fraction [µmol/mol]
CO	0.1 – 1.0
H_2S	0.02 – 0.5
O_2	1 – 10
H_2O	1 – 10

- Discussion
  - Number of participants: limited to 12
  - Selection of participants?
  - List of compounds, target amount fraction and cylinder type (valve, volume, pressure)
  - Delay to perform analysis: < 8 weeks
  - Possibility to keep intercomparison sample: yes/No
  - Anonymous?

Project Team

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NPL
National Physical Laboratory

FORCE TECHNOLOGY

RI. SE

NEN

CEM
CENTRO ESPAÑOL DE METROLOGÍA

VSL
Dutch Metrology Institute

METAS

ITM POWER
Energy Storage | Clean Fuel

AIR LIQUIDE

SINTEF

THE LINDE GROUP
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Materials Science & Technology

CASCADE TECHNOLOGIES

CEſAME-exadébit SA

FUNDACION PARA EL DESARROLLO DE LAS NUEVAS TECNOLOGIAS DEL HIDRÓGENO EN ARAGÓN

nel
flow measurement services

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THANK YOU