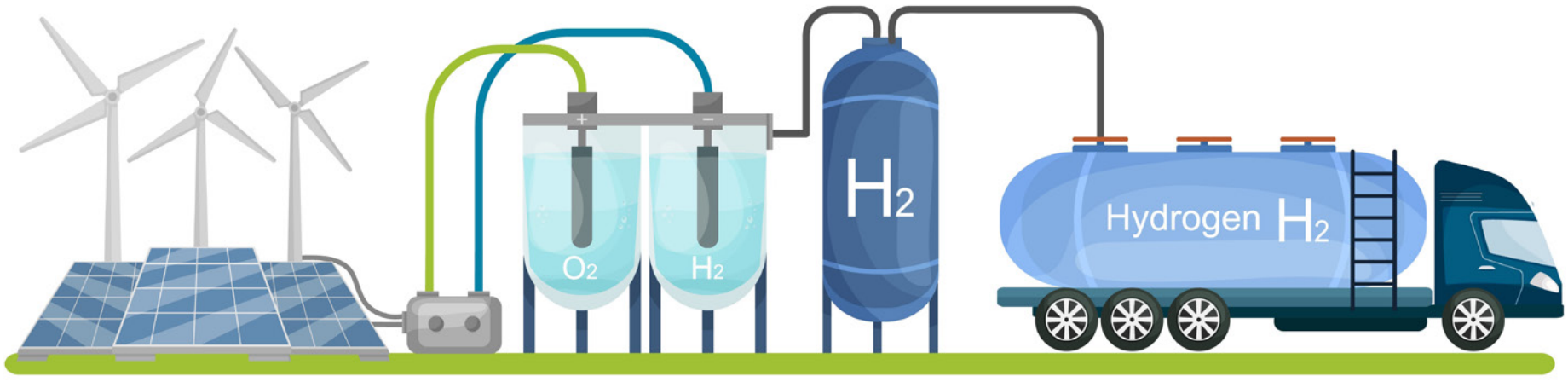
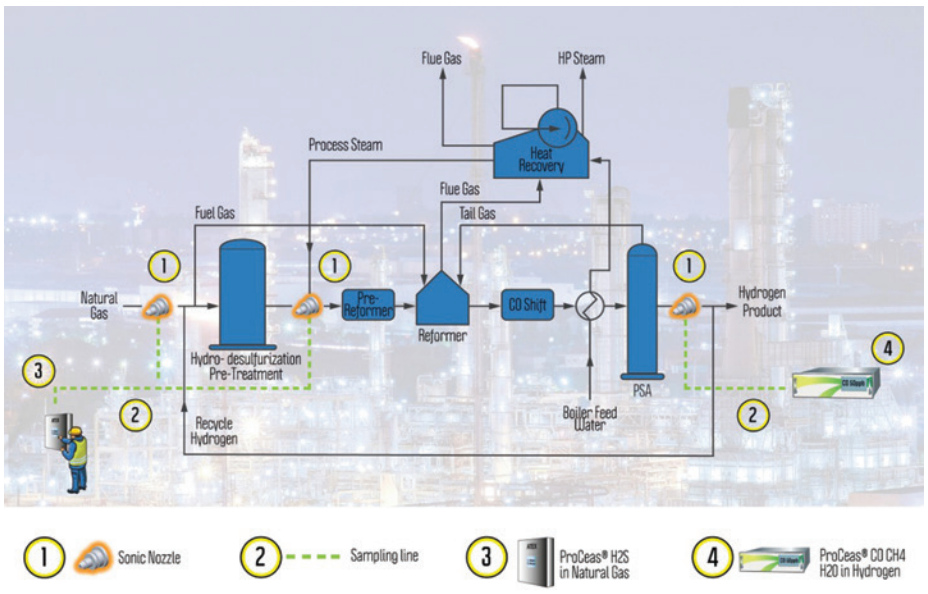


COMBINATION OF OFCEAS SPECTROSCOPY AND LOW PRESSURE SAMPLING, FOR IMPURITIES MEASUREMENT IN HYDROGEN PRODUCTION AND STORAGE

In the energy sector, where clean resources are increasingly sought, hydrogen production and fuel cell development seem most promising. A fuel cell generates electricity from an electrochemical reaction. Hydrogen and oxygen are combined (hydrogen oxidation) to generate a continuous current of electricity, heat, and water vapor. Consequently, there is no CO_2 emission and fuel cells allow an indirect valorization of renewable resources, depending on the production process. Nowadays, fuel cells can be used in various applications like portable power, backup power (hospitals, data centers, etc.) transportation applications (cars, buses, trucks, trains, etc.) and many others.

There are different existing ways of producing hydrogen. The most common production technic is petrochemical processing like steam methane reforming which consists in an endothermic reaction between hydrocarbons (from natural gas) and water vapor.



Steam Methane Reforming process description, and typical ProCeas analysers implementations

ISO 14687-2019 list of impurities

Constituents	concentration max. (ppm)
H_2O	5
Total Hydrocarbons (except CH_4)	2
O_2	5
He / N_2 / Ar	300
CH_4	100
CO_2	2
CO	0,2
Total sulphur	0,004
HCHO	0,2
HCOOH	0,2
NH_3	0,1
Halogenated	0,05

A cleaner production technic is the electrolysis which decomposes water into oxygen and hydrogen by applying an electrical current between two electrodes. Others technologies are also under development like hydrogen production from biomass (cf. Haffner Energy IPO in February 2022).

Though the diversification of production technics represents an opportunity for the long term development of the hydrogen market, they create different types of impurities (which may vary depending on the considered H2 production processes) within the supplied gas. Indeed, it has been shown that even very low concentrations of these impurities can cause non-negligible damages to components, and in particular to fuel cells.

Researches resulted in the publication of a new ISO Standard – ISO 14687, where multiple molecules have been identified as hazardous for fuel cells. Thus, highly restrictive concentration thresholds have been determined for numerous gases such as H_2S, HCHO, HCOOH, NH_3, CO, HCl, etc. In particular, when internal combustion engines can tolerate low gasoline quality, these hydrogen impurities need to be monitored in order to prevent fuel cells from being prematurely damaged and to avoid catalyst poisoning.

A European project, Metrology for Hydrogen Vehicle (MetroHyve), led by a partnership between the National Physical Laboratory (NPL, UK), the Dutch Metrology Institute (VSL, NL) and the Research Institute of Sweden (RISE, Sweden), has evaluated a novel analyzer for hydrogen purity with respect to ISO 14687. The study led to the validation of an OFCEAS-GC combination for the monitoring of all determined impurities.

Indeed, for trace gas analysis, AP2E double technology (OFCEAS and LPS) reveals its strongest advantages.

AP2E standard ProCeas H2 PURITY analyzer, in rack integration

OFCEAS or Optical Feedback Cavity Enhanced Absorption Spectroscopy, is a gas analysis technology developed by the University Joseph Fourier (Grenoble, France). OFCEAS gathers traditional infrared components such as a laser, a set of optics, a measuring chamber and a photodiode (laser detector). However, it differs on many other ways with older infrared technologies.

First, it is called enhanced cavity as the measuring chamber (or cavity) in which the sample is analyzed is equipped with high reflectivity mirrors (>99,99%). This means that the laser beam is kept back and forward within the cavity before getting out. Thus, the optical path length provided reaches up to 50 km (against only 1 to 10m for traditional IR technologies). There are therefore five thousand times more absorption. Moreover, Beer-Lambert's law relates the absorbance of light A_λ to the properties of the gas through which the light is travelling. It is described as followed:

$$A_\lambda = C\, L\, \varepsilon_\lambda$$

C is the concentration of the studied compound, L the optical path length, ε_λ is the molar attenuation coefficient. As a result, it is possible to measure five thousand times lower in concentration. This is the reason why AP2E analyzers can measure down to ppb or ppt concentrations.

Second part of the OFCEAS patent is the feedback principle. A very small amount of the emitted radiation is sent back from the chamber to the laser diode, enabling the tuning of the laser and the cavity, creating a resonance phenomenon. Global laser intensity is therefore fully focused on the studied wavelength, which prevent from side noises. The consequence of this phenomenon is the identification of intense absorption peaks with narrow spectral width. This feature allows multi-components analysis with one laser source and combination of several lasers in one analytical unit.

Moreover, during a measurement, the laser diode current is slightly modified to get 200 resonance phenomena close to the studied wavelength. This means a very high-resolution spectrum of 200 peaks, for a global resolution of 1 picometer, where NDIR and FTIR technologies only reaches respectively 20 nm and 2nm.

Consequently, by using OFCEAS technology, all absorption peaks are separated, there is negligible cross-interferences. And it allows advanced levels of detection.

AP2E developed a second patented technology (coupled to OFCEAS) called low pressure sampling. LPS is a sampling technique, which consists of maintaining the global analysis solution at low pressure, generally between 20 to 100 mbar absolute. This global analysis solution gathers an inlet probe (filter and sonic nozzle), the sampling line, the measuring chamber of the analyzer and a vacuum pump at the exhaust. The sonic nozzle is like a pinhole from 50 to 150 µm, generating important head losses and ensuring the gas to reach sonic velocity. Coupled to the vacuum pump, it regulates global pressure and flow rates of the global analysis system.

The first benefit is that gas interactions are reduced at low pressure. It has a direct effect on the shape of absorption peaks. In low pressure the pics become sharper, which still contribute to reduce cross-interferences and get a high-resolution spectrum. The gas consumption is very low compared to traditional sampling techniques, which is critical for analyzing canister of samples gas from hydrogen refueling stations. Moreover, gas velocity is multiplied by the ratio between inlet pressure and sampling pressure. Thus, it considerably lowers the overall response time.

In conclusion, this double-patented technology allows AP2E to position itself as a standard way of measuring H2 impurities in order to meet ISO 14687 requirements. The limits of detection (LOD) at 3σ 60s are at least twenty times lower than concentrations thresholds for each compound. Consequently, AP2E is able to measure most of the impurities (all of them by combination with gas chromatography) of the ISO 14687 standard by proposing a global analysis solution with negligible cross-interferences (where other IR technologies may have issues with 100ppm CH4 max content), fast response time, low LOD and a low gas consumption.

AP2E is taking part in multiple European working groups, like Metrohyve (NPL/NEL) and Hydrogen (LNE). They have numerous installations running worldwide for most important H2 market players in the industry (Air Liquide, SHELL, ENGIE, etc.) and in research (ZSW, CEA, RISE, SUPELEC, etc.).

New ISO 14687 standard for impurities content in H_2 and associated LODs from AP2E ProCeas H_2 PURITY analyser

Component	New ISO 14687 limits (ppm)	ProCeas® Limit Of Detection 3σ 60s (ppm)
H_2O	5	0.02
CH_4	100	0.001
O_2	5	0,1
CO_2	2	0.01
CO	0.2	0.001
H_2S	0,004	0.001
COS	0,004	0.001
HCHO	0,2	0.001
HCOOH	0,2	0.01
NH3	0,1	0.001
HCl	0,05	0.001

Source:

https://iopscience.iop.org/article/10.1088/1361-6501/ab7cf3

https://www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-hydrogen-vehicles/?L=0&tx_eurametctcp_project%5Baction%5D=show&tx_eurametctcp_project%5Bcontroller%5D=Project&cHash=306d1f42e20989c0b2658abf0f76c8ca

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