GLOBAL FLOW MEASUREMENT WORKSHOP
measuring for the energy transition

Combination of OFCEAS Spectroscopy and Low-Pressure Sampling, for impurities measurement in hydrogen production & storage

Etienne SMITH, AP2E a DURAG Group company

Introduction:

Currently hydrogen and fuel cell developments are growing rapidly.

It has been demonstrated that even very low concentrations of gas impurities can cause significant damages, in particular to fuel cells. Thus, researches resulted in the publication of a new ISO standard – ISO 14687, where multiple molecules have been identified as hazardous, and highly restrictive concentration thresholds have been determined.

The 14 gas impurities listed in ISO 14687:2019 resulted to be very challenging for most analytical laboratories, and this resulted in the need of development of a new analytical solution. AP2E, a manufacturer of laser-based gas analyzer, developed a solution combining its two patents OFCEAS and LPS.

Constituents	grade D
Hydrogen fuel index (minimum mol fraction)	99,97%
Total non-hydrogen gases (maximum)	300 µmol/mol
Individual contaminants	Max concentration (µmol/mol)
He / N2 / Ar	300
CH4	100
H2O / O2	5
Total Hydrocarbons (except CH4) / CO2	2
CO / HCHO / HCOOH	0,2
NH3	0,1
Halogens compounds	0,05
Total sulfur	0,004
Maximum particulate concentration	1 mg/kg

Table 1: Specifications of hydrogen Grade D following ISO 14687:2019

OFCEAS:

OFCEAS or Optical Feedback Cavity Enhanced Absorption Spectroscopy, is a gas analysis technology developed by the University Joseph Fourier (J. Morville, 2005). Its enhanced-cavity is equipped with highly reflective mirrors (>99,99%), which allow the laser beam to achieve a pathlength of 5 to 50 kilometers. OFCEAS essentially differs from the older TDLAS technologies by its feedback principle: a part of the emitted radiation is returned from the chamber to the laser, enabling the tuning of the laser and the cavity, creating a resonance phenomenon. 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 down to ppb concentration and combination of several lasers in one single analytical unit.

LPS:

LPS or Low-Pressure Sampling, is an AP2E patented sampling technique. This principle consist of critical orifice at the inlet; and a vacuum pump at the outlet of the analyzer. The critical orifice limits the inlet gas flow and the vacuum pump therefore apply an under pressure on the entire sampling system, maintaining pressure under 100mbar absolute. Given that, the transfer time is shorten, the sample flow is reduced (<20l/h) allowing measurements on small gas cylinders, and the interferences between absorption peaks are minimized.

Results:

In the scope of the European project "METROHYVE", AP2E investigated different wavelengths, to find optimal lasers to cover the analytical needs of ISO 14687:2019. The goal was to find wavelengths which can measure correctly the 14 gas impurities, with correct repeatability at the threshold of the ISO standard, and without cross interferences from the other gases.

This investigation resulted in the definition of 3 standard analyzer racks.

The first analyzer is dedicated to H2O, CH4, CO2, CO, HCHO, HCOOH, NH3.

Component	ISO 14687 limits (ppm)	ProCeas® LOD 3σ 60s (ppm)	ISO threshold / LOD
H2O	5	0.1	x 50
CH4	100	0.05	x 2000
CO2	2	0.02	x 100
CO	0.2	0.002	x 100
HCHO	0,2	0.01	x 20
HCOOH	0,2	0.01	x 20
NH3	0,1	0.005	x 20

Table 2: ProCeas H2 Purity – module 1

The second analyzer is dedicated to sulfur and halogenated compounds.

Component	ISO 14687 limits (ppm)	ProCeas® LOD 3σ 60s (ppm)	ISO threshold / LOD
H2S	0,004	0.001	x 4
H2O	5	0.05	x 100
COS	0,004	0.001	x 4
HCl	0,05	0.001	x 50

Table 3: ProCeas H2 Purity – module 2

The third analyzer is dedicated to O2. And can be complemented by other lasers on demand to measure gases such as HF, HBr, or CS2

Component	ISO 14687 limits (ppm)	ProCeas® LOD 3σ 60s (ppm)	ISO threshold / LOD
O2	5	0.1	x 50

Table 4: ProCeas H2 Purity – module 3

At the conclusion of METROHYVE, a typical laboratory setup was proposed, with a combination of OFCEAS gas analyzers with a Gas Chromatograph.

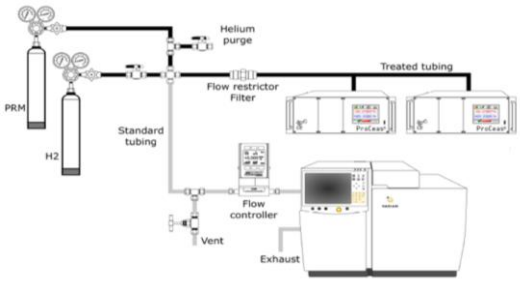

Fig. 1: METROHYVE laboratory setup proposal (K. Arrhenius et al, 2020)

Conclusion:

AP2E has developed 3 standard analytical modules, able to measure 10 gas impurities among the 14 gases listed in ISO 14687:2019. The final solution is quite compact, user friendly, and price competitive versus other comparable solutions such as Mass Spectrometers. The only limitation of the OFCEAS is that it cannot measure non infrared absorbing gases (N2/He/Ar), and total hydrocarbons, but this can be easily done by a complementary GC/FID-TCD already present in most analytical laboratories, limiting the investment cost and redundancy in analytical capacities. The OFCEAS gas analyzers are already installed in more than 50 laboratories worldwide for ISO 14687:2019, making it a field proven solution for hydrogen grade D purity control. This optimization work is also promising for other applications, like measurement of gas impurities in CO2 for Carbon Capture.

References:

Morville, J., Kassi, S., Chenevier, M., and Romanini, D.: Fast, low noise, mode-by-mode, cavity-enhanced absorption spectroscopy by diode-laser self-locking, Appl. Phys. B, 80, 1027–1038, doi:10.1007/s00340-005-1828-z, 2005.
K. Arrhenius, O. Büker, A. Fischer, S. Persijn, and N. D Moore: Development and evaluation of a novel analyser for ISO14687 hydrogen purity analysis Meas. Sci. Technol. 31 075010, DOI 10.1088/1361-6501/ab7cf3, 2020.