

Hydrogen Fuel Quality Control and Process Monitoring by Direct, Real-time Mass Spectrometry

Fuel cell electric vehicles (FCEV) are supposed to be a real breakthrough for e-mobility and could represent 32% of the fuel demand by 2050. This goes along with directives and requirements for the quality control and process monitoring of hydrogen in production, transport and fuel cells. Selected ion flow tube mass spectrometry (SIFT-MS) can play an important role by providing rapid, real-time and sensitive monitoring of volatile contaminants in hydrogen.

Introduction

For the purity check and analysis of hydrogen, several standards exist already (ISO 14687, SAE J2719, ISO 19880-8, EN 17124) for analytical technologies like CRDS, GC with various detectors, TD-GC/MS, IC or QCM. Gaps of those may be found for sensitivity and throughput. SIFT-MS can be a valuable addition to this toolbox for certain contaminants due to the capability of a direct and fast analysis.

Shown here here is the rapid check of compounds like formaldehyde, formic acid and ammonia in the range of 20nM - 1 μ M as well as CO₂ in H₂ fuel. Measurements are assessed against reference materials to ensure the accuracy of the results.

Method

SIFT-MS uses soft chemical ionization (CI) for the generation of mass-selected product ions to rapidly quantify volatile compounds down to pptV concentrations. A uniquely wide range of eight reagent ions (H₃O⁺, NO⁺, O₂⁺, O⁻, OH⁻, O₂⁻, NO₂⁻ and NO₃) obtained from a microwave discharge of moist air are applied in the commercial Voice 200ultra SIFT-MS instrument. The ions interact with volatile compounds and other trace analytes in well-controlled ion-molecule reactions, allowing for fast, real-time analysis at ultra-trace levels without pre-concentration or the need of front-end separation. Rapid switching between reagent ions provides high selectivity, because the multiple reaction mechanisms provide additional independent measurements of each analyte. The multiple reagent ions also help to remove uncertainty from isobaric overlaps in mixtures containing multiple analytes. Identification and quantification is enabled by matching the data with library entries.



Fig. 1: Voice200 ultra SIFT-MS

Results

Fig. 2 demonstrates the analysis of ammonia in H₂. Accuracy of the quantification is within 10% of the reference, and the limit of detection (LOD) is 20 nmol/mol. The runtime is just 20 min with 20L of total gas volume.

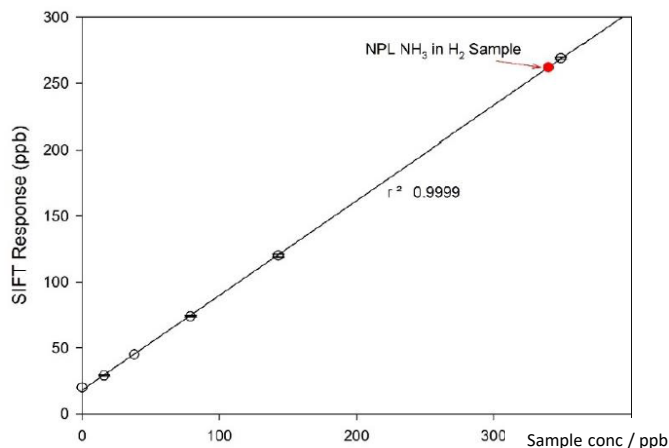
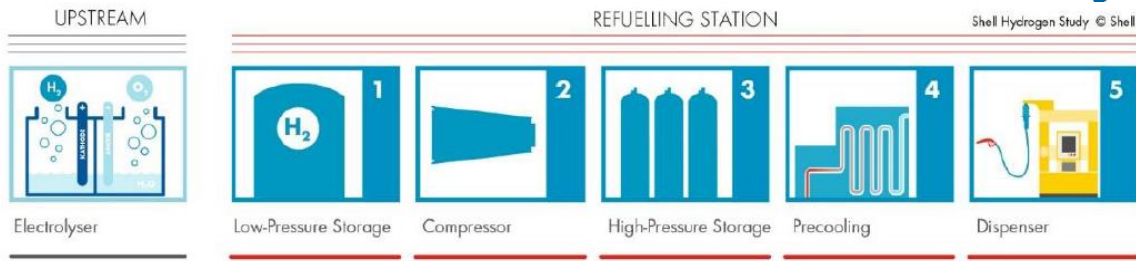


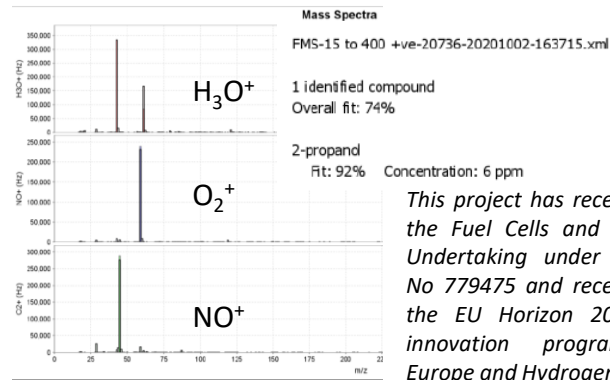
Fig. 2: Quantification of ammonia across several orders of magnitude. The red dot marks the match with the NPL standard. Unpublished data from Thomas Bacquart (NPL) and Matt Langley (CSIRO).



Fig. 3: Process of a hydrogen fueling station (taken from Shell Hydrogen Study)



Possible contaminations along a supply chain (fig. 3) can be identified by SIFT-MS in minutes to < 1h and quantified within the correct order of magnitude. Fig. 4 shows the identification of an unknown. The non-methane total hydrocarbon analysis provided a value of > 2µmol/mol. The use of three different reagents identified the compound as 2-propanol.



This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 779475 and receives support from the EU Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.

Fig. 4: Identification of 2-propanol by the combined use of the reagent ions H_3O^+ , NO^+ , O_2^+ .

Contaminants can be present in the H₂ and be transferred to the stack. CO is prevalent in some H₂ production process and a critical contaminant which absorbs on the fuel cell catalyst and poisons the system. This leads to performance loss, reduced lifetime and system failure. Understanding the poisoning mechanism is critical to ensure the lifetime of the vehicles

Challenges (see fig 5):

- Quick conversion of CO into CO₂
- Presence of CO₂ from air
- High humidity (60% RH)
- No study monitored real time the oxidation of CO into CO₂ in fuel cell stack.

Proposal:

- Use ¹³CO to monitor conversion into ¹³CO₂
- SIFT-MS suitable for this analysis

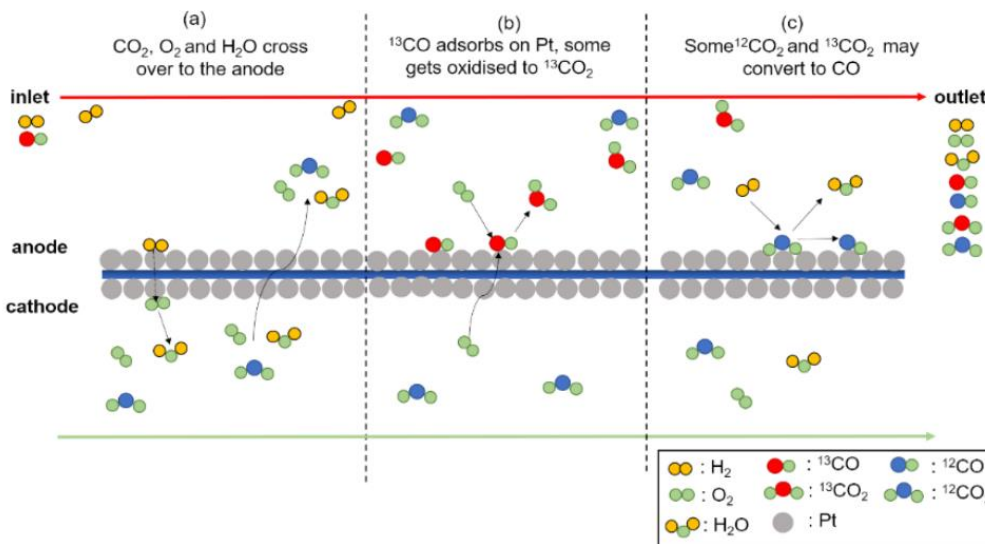


Fig. 5: generation of CO in the electrolysis.

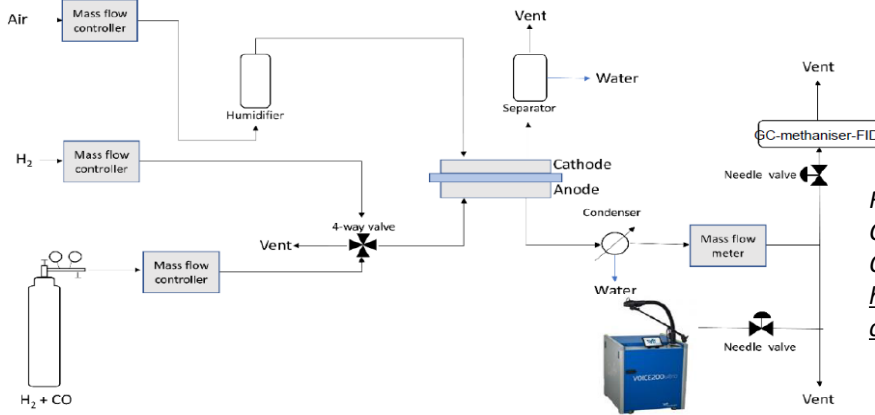


Fig. 6: Experimental setup of CO and CO₂ analysis by the negative reagent OH⁻. For more details see: <https://www.sciencedirect.com/science/article/pii/S2666248520300366>

Fig. 6 shows the setup for CO and CO₂ analysis by GC-FID and SIFT-MS. Preparation of gravimetric standard was done using ¹³CO to contaminate the system. Gas standards were prepared with CO₂ and ¹³CO₂ in hydrogen (dry gas). The gas analysis is built at fuel cell outlet (single cell) after the dryer (6 °C). SIFT-MS performed ¹³CO₂ and ¹²CO₂ analysis using negative ion OH⁻ (Helium carrier) with product ions at m/z -61 and -62. GC-methanizer-FID were applied in parallel to measure CO and total CO₂.

The ¹²CO₂ and ¹³CO₂ profiles can be discriminated (fig. 7), and the behavior is coherent with oxidation of ¹³CO in ¹³CO₂. A clear correlation to the impact on a single cell (voltage decay) can be observed.

Fig. 7: Emission of CO and CO₂ as a function of cell voltage and catalyst surface coverage.

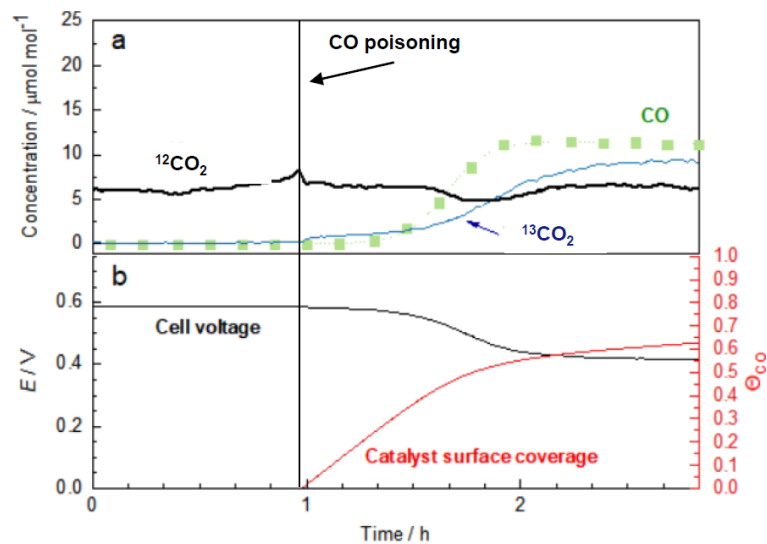
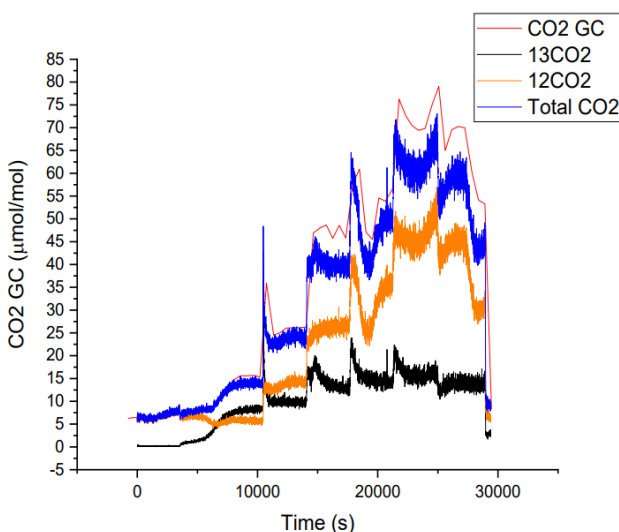


Fig. 8 shows the comparison of the quantitative results between conventional GC and SIFT-MS. SIFT-MS can distinguish ¹³CO₂ and ¹²CO₂

Fig. 8: External SIFT-MS calibration using NPL PRM for CO₂ and ¹³CO₂ in hydrogen plus correction between dry/wet gas.



Toluene contamination of fuel cell - Online measurement on system with recirculation loop (fig. 9).

Operating short stack with constant conditions: ~99% enrichment are expected. Toluene inlet provides 2.9 $\mu\text{mol}/\text{mol}$ contamination in H_2 (which is 10x of the ISO14687 limit).

With positive reagent ions toluene is detected by NO^+ reaction at m/z 92. As by-products, methylcyclohexane is detected by NO^+ reaction at m/z 97. Nearly all toluene is hydrogenized. The quantification was performed only preliminary with no check for partially saturated intermediates. The contamination of the stack showed a strong dependence on the present CO concentration. With SIFT-MS, a true real-time monitoring of the fuel cell contamination was possible.

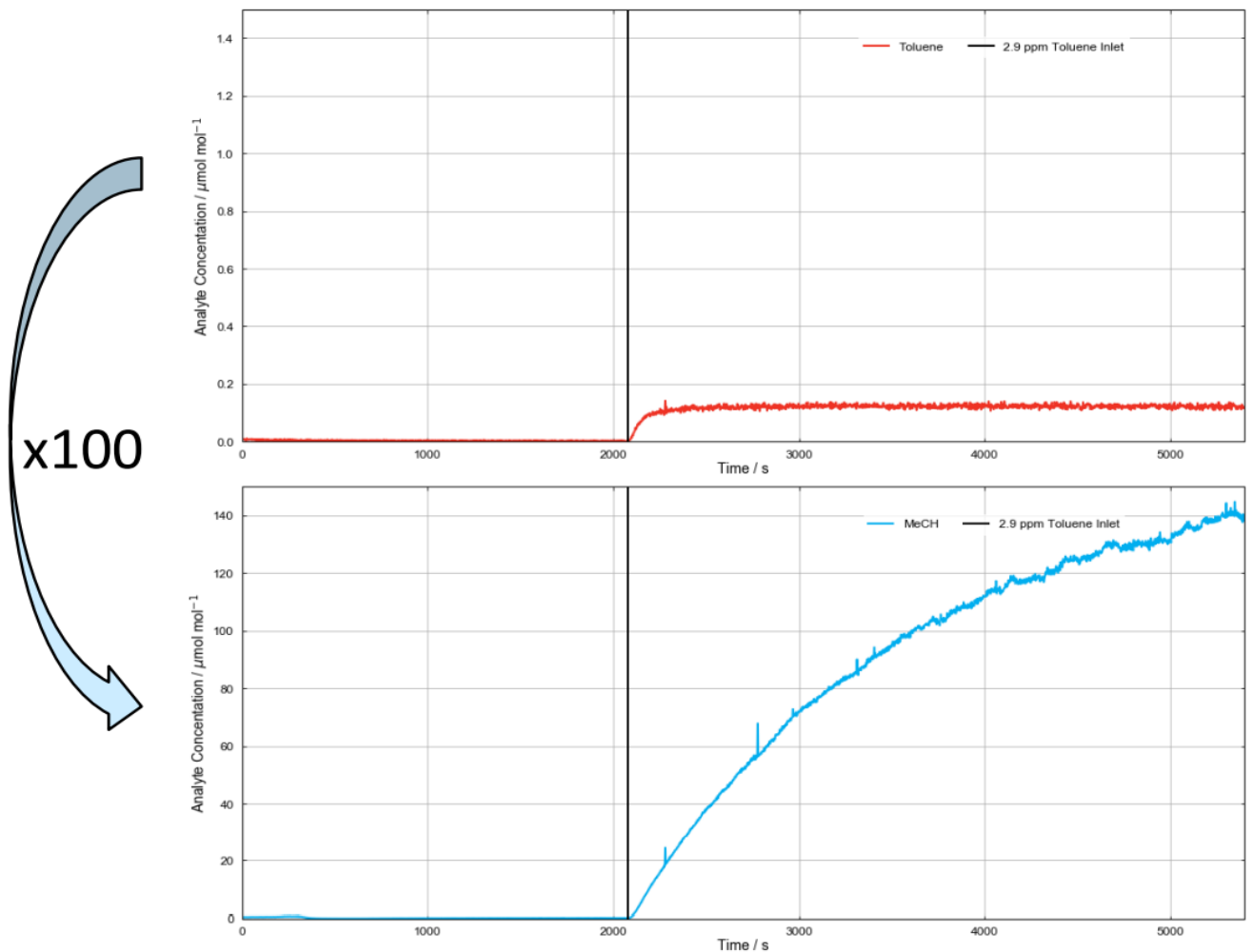


Fig. 9: time course of the stack contamination by toluene and MeOH.

Table 1: ISO 14687:2019 and corresponding SIFT-MS data. “Y” marks those compounds which can be analyzed by SIFT-MS. Others are under development.

Y/ N	Compound	Max. allowed conc.	Notes on ISO standard requirements	SIFT-MS data
N	H ₂ O	5 ppm		Instrument not sufficiently accurate for H ₂ O
Y	Total hydrocarbons	2 ppm	Incl. oxygenated species, excl. methane	Determined as sum parameter
(N)	Methane	100 ppm		Cross talk with other compounds
N	Oxygen	5 ppm		-
N	Helium	300 ppm		-
N	Nitrogen	300 ppm		-
N	Argon	300 ppm		-
Y	CO ₂	2 ppm		Detected with negative reagent ions
N	CO	0.2 ppm		-
	Total sulphur			
Y	H ₂ S	0.004 ppm	Sum of these four entries	Determined individually and summed up. No sum parameter available for mercaptans alone.
Y	COS	0.004 ppm		
Y	CS ₂	0.004 ppm		
(Y)	Mercaptans	0.004 ppm		
Y	Formaldehyde	0.2 ppm	Sum of CO, formaldehyde and formic acid	Formaldehyde and formic acid determined individually and summed up.
Y	Formic acid	0.2 ppm		
Y	Ammonia	0.1 ppm		OK
(Y)	Halogenated compounds	0.05 ppm	HCl + organic R-Cl	Determined individually and summed up
N	Max. particulates	1 mg/kg		Solids are not detectable

