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Evaluation of Selectivity and Resistance to Poisons of Commercial Hydrogen Sensors

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European Commission

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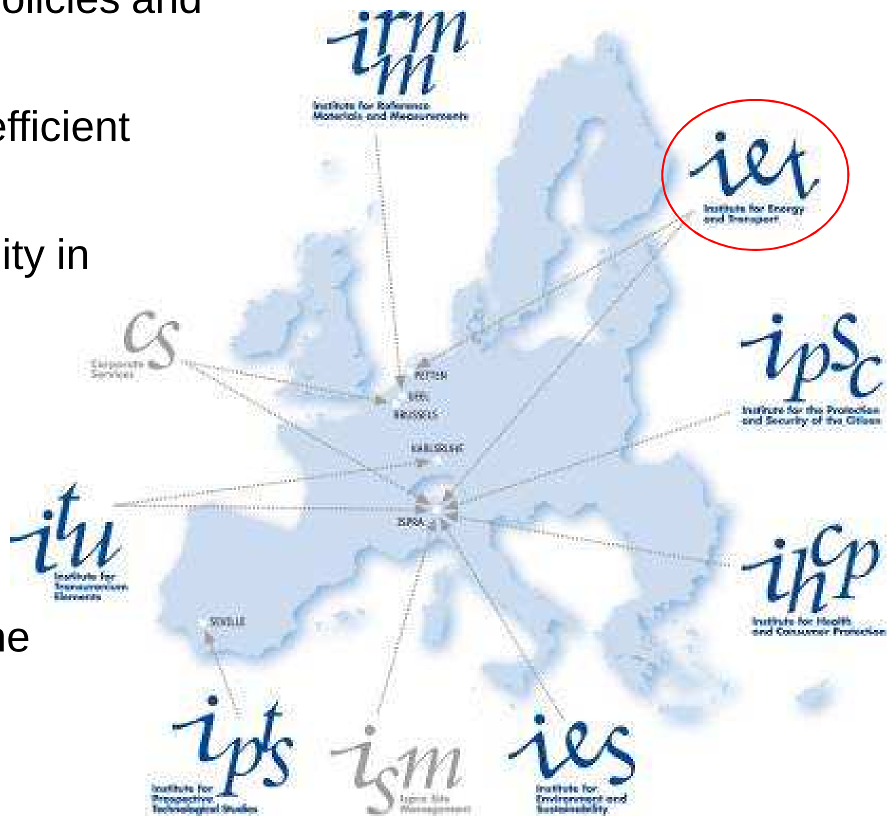
2) transport - to foster sustainable and efficient mobility in Europe.



Independent of private, national, financial or commercial interests

Cooperation with leading scientific organisations in the Member States, Associated Countries and worldwide.

Joint Research Centre

JRC- sensor testing facility (SENTEF)

- Performance testing of H_2 Safety Sensors
- Comparison of different sensing technologies
- Influence of ambient parameters/contaminants
- Sensor response/recovery time measurement

- Temperature: -40°C → +130°C
- Pressure: 1 → 250 kPa
- RH: 10% @ -40°C, 99% @ 60°C
- 4 MFCs for inlet gases (H_2, CO, CH_4, CO_2, SO_2,…)
- GC Gas analysis

→ **collaborations** NREL

L. Boon-Brett, J. Bousek, P. Castello, O. Salyk, F. Harskamp, L. Aldea, F. Tinaut, IJHE, Volume 33, 7648-7657 2008

Mature technologies for sensing H_2

Thermal Conductivity (**TCD**)	H_2: highest thermal conductivity of all known gases. $[H_2] \uparrow \longrightarrow$ **T** $\uparrow$ at sensing point, detected through a Wheatstone bridge.
Catalytic (CAT)	A sensing element detects the **heat of combustion** of H_2 with O_2 at the Pd/Pt catalyst.
Semiconductive Metal-Oxide (MOX)	Hydrogen gas reacts with chemisorbed O_2 in a semiconducting material, such as tin oxide, and changes the **resistance** of the material.
Electro-chemical (EC)	Oxidation of H_2 at the sensing electrode producing a **current** proportional to $[H_2]$. Counter reaction at the cathode (reduction of O_2)
Metal Oxide semiconductor (MOS)	3 layers structure: metal-insulator (oxide)-semiconductor. H_2 split at catalytic metal (Pd) giving raise to a H-dipole layer (at the interface) $\longrightarrow$ **work function** changes
Pd Thin Film (PTF)	Most common relate the **resistance** of a Pd-based thin film to the external concentration of H_2

Developping techniques: Optical, acustic, mechanical…

Cross sensitivity / poisons issue

Cross-sensitivity (i.e. selectivity): ability of a sensor to respond to the target analyte, regardless of the presence of other species.

Cross-sensitivity and resistance to poisons are considered main issues by sensor *end-users* because can lead to:

Undetected hydrogen leaks, with serious safety consequences (*false negative*)

False alarms, with economic damage (*false positive*)

We use *ISO 26142* as a guide to define the effect of:

Interferents, transient effect on the sensor performances;

Poisons, the effect persist after exposure.

Strategies for selectivity

TCD	Responding to any species with a thermal conductivity different than air. Practically only He and few other species at high concentration. **No poison effect** expected (no chemical reaction is involved)
CAT	In principle may respond to any combustible gases. Selectivity: **Pd catalyst** + **filters/ molecular sieve coatings**.
MOX	Poor selectivity to H_2, i.e. responding to CO, CH_4, H_2O. Various strategies to increase selectivity: adjusting the MOX **crystal structure** and composition with **dopants**; optimising the sensing material **operating temperature** for H_2 detection; covering the surface with a **silica layer.**
EC	**Membranes**, (hindering diffusion of gasses ≠ H_2 into the electrode); **Selective materials** (for H_2) catalysing the electrochemical reactions.
MOS	Selectivity assured by the use of specific catalytic metals (**Pt, Pd**).
PTF	**Pd** surface selective to H_2; **Protective membranes** (e.g. polymers like PTFE) against poisons (CO, SO_2, H_2S and Si-based compounds).

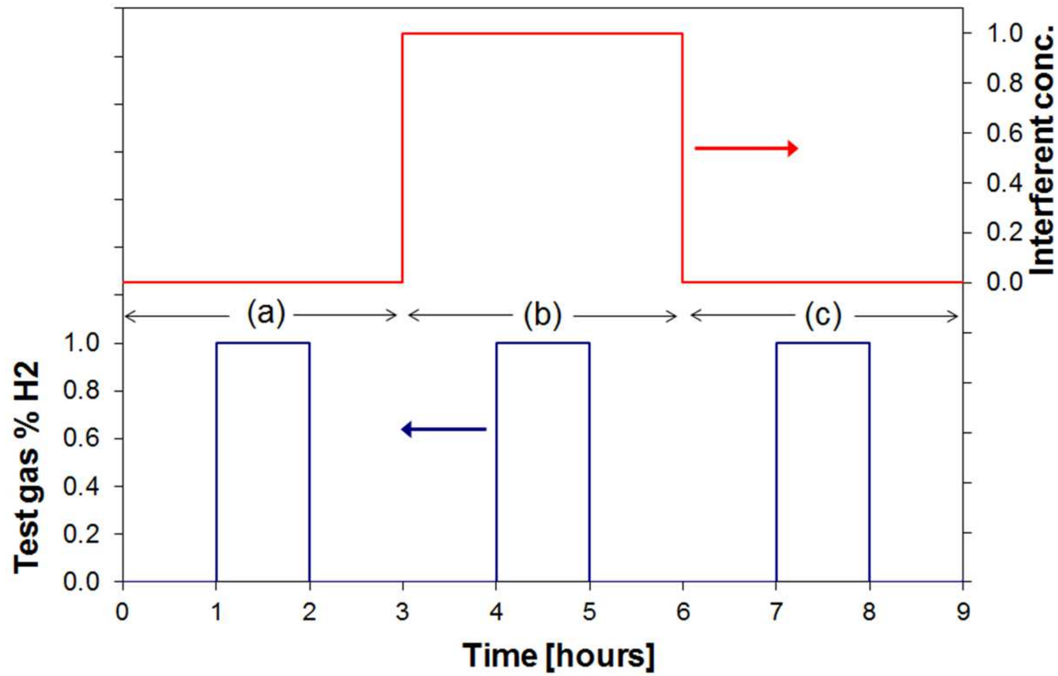
Exposure profile

a) Exposure to 1vol% H_2 in air (**control measurement stage**)

b) Exposure to 1vol% H_2 in presence of the interferent "i" (**cross-sensitivity measurement stage**)

c) Exposure to 1vol% H_2 in air (**recovery stage / poison effects**)

The diluent gas is clean air.

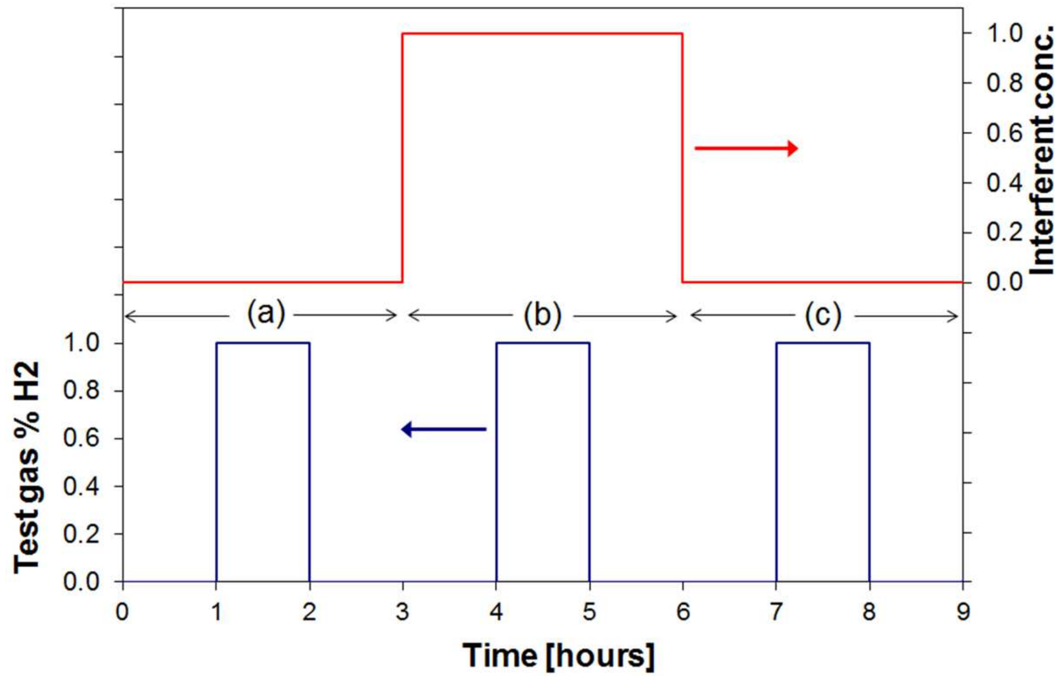


Exposure profile for the cross sensitivity test.

Exposure profile

Gas species "i" and test concentrations

Species "i"	c [ppm]	
CO_2	5000	level allowed by US OSHA
CH_4	10000	20% LEL
CO	50	level allowed by US OSHA
SO_2	500	ISO standard



Exposure profile for the cross sensitivity test.

The response to other species is being tested.

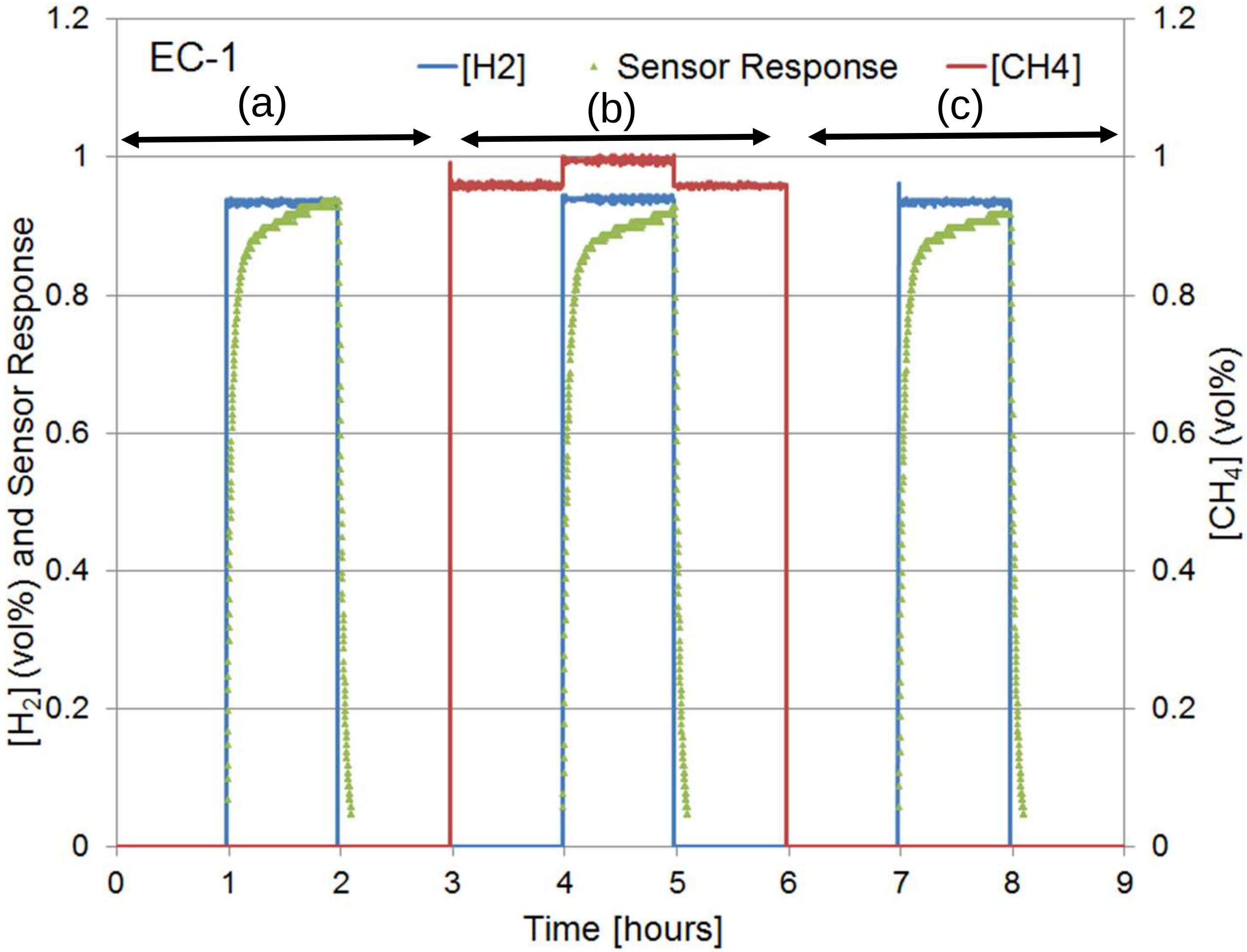
EC platform vs. CH_4

a) Reference

b) Cross sensitivity effect

c) Poison effect

No effect!



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EC platform vs. SO_2

Net response to the interferent

$$X_0^i = \frac{R_i - R_0}{R_H - R_0} = 0.06$$

Increment of the sensitivity to H_2 in presence of the interferent

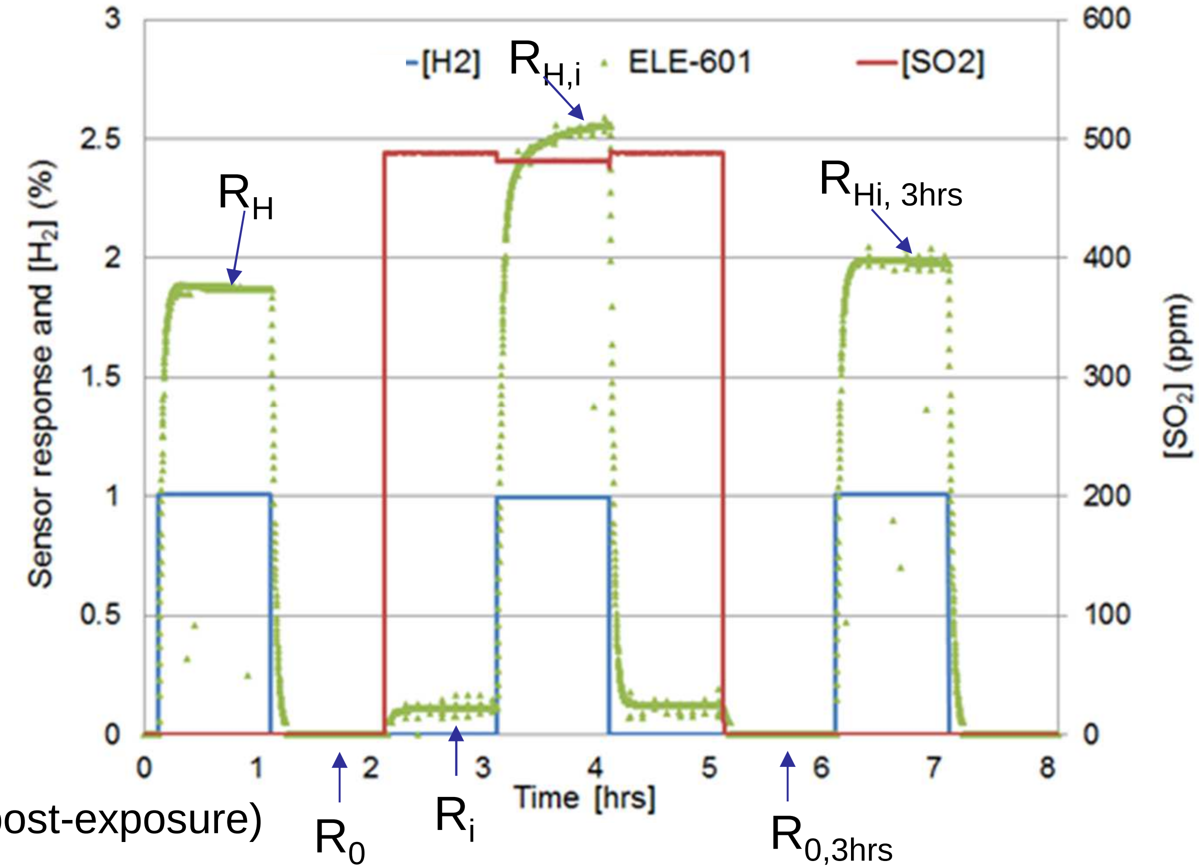
$$X_H^i = \frac{R_{H,i} - R_i}{R_H - R_0} - 1 = 0.30$$

Change in the baseline after 3h exposure

$$P_0^i = \frac{R_{0,3hrs} - R_0}{R_H - R_0} = 0$$

Increment of the sensitivity to H_2 (post-exposure)

$$P_H^i = \frac{R_{H,3hrs} - R_0}{R_H - R_0} - 1 = 0.06$$



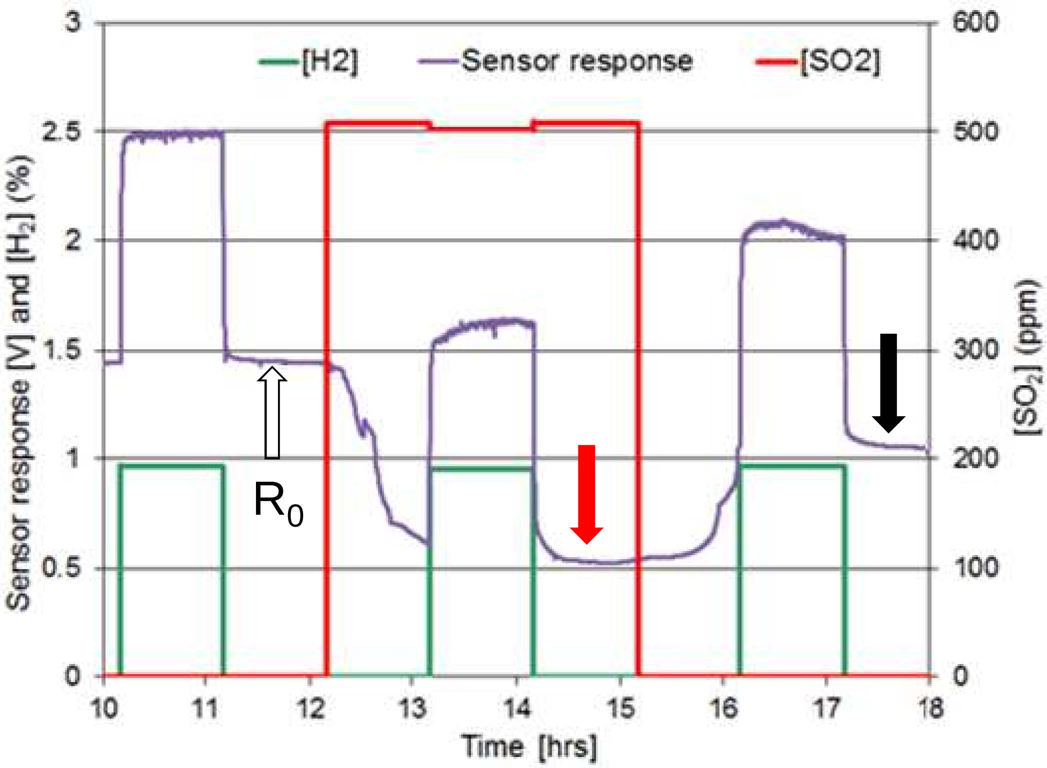
Catalytic platform

Cross sensitive to SO_2

Species	X_0	X_H
500 ppm SO_2	-0.88 ± 0.05	0.05 ± 0.05

500 ppm SO_2: detrimental on the sensor output.
Partially recovered by exposure to clean air

Species	P_0	P_H
500 ppm SO_2	**-0.36 ± 0.05**	-0.05± 0.05



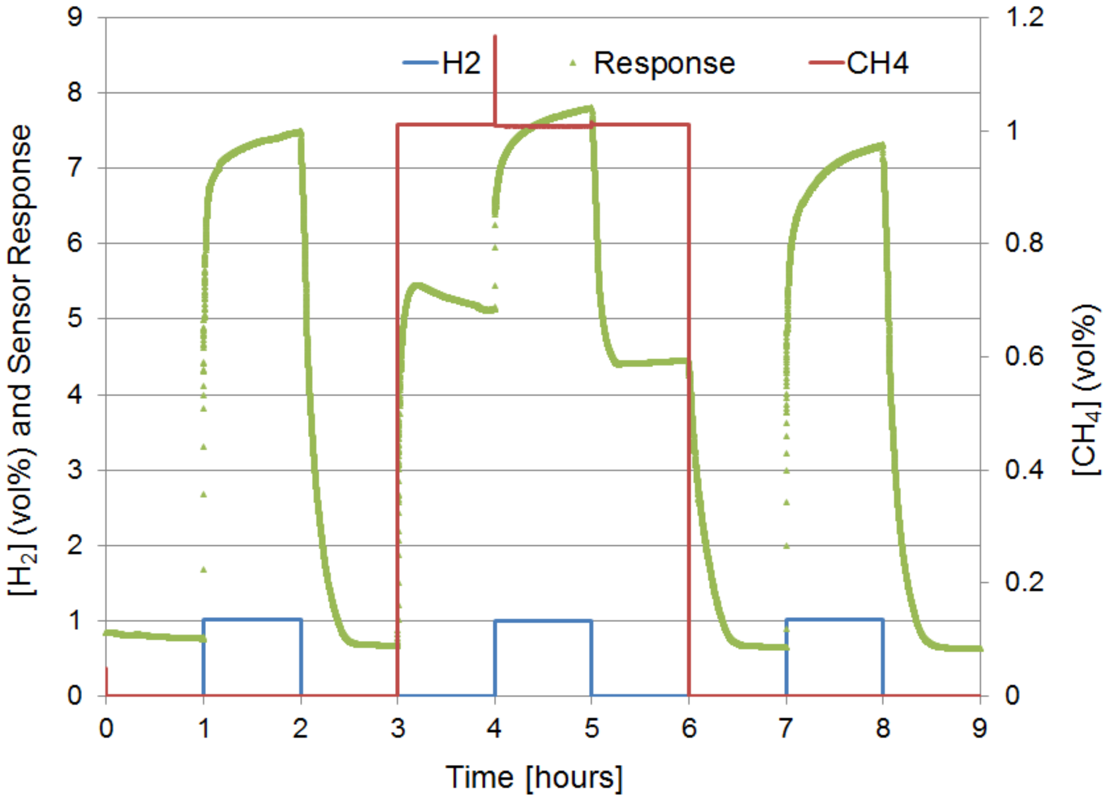
CAT response during the exposure profile with 500 ppm SO_2

MOX platform

Negligible effect of CO and CO_2

Cross sensitive to CH_4: *promoter* for the absolute response; *inhibitor* for the net response.

Species	X_0	X_H
1% CH_4	0.65 ± 0.05	-0.6 ± 0.1



MOX response during the exposure profile with 1.0 vol% methane.

TC platform

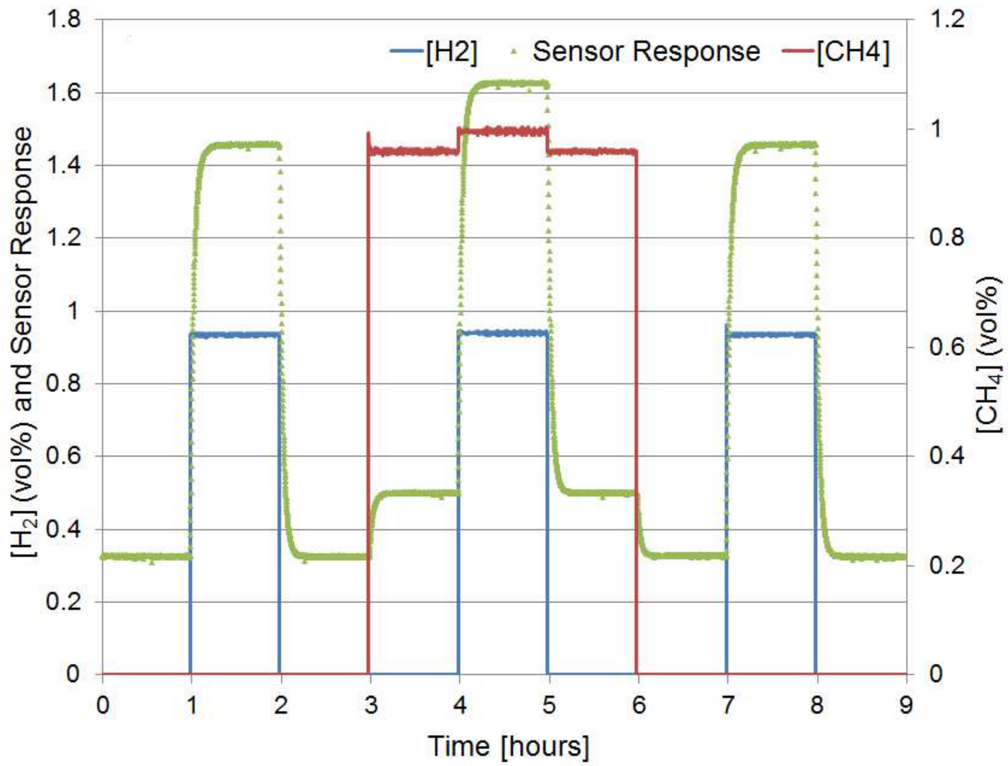
No poison effect was found.

Negligible X_H for any gas tested.

$K_{CH4} > K_{air} \rightarrow X_0 > 0$

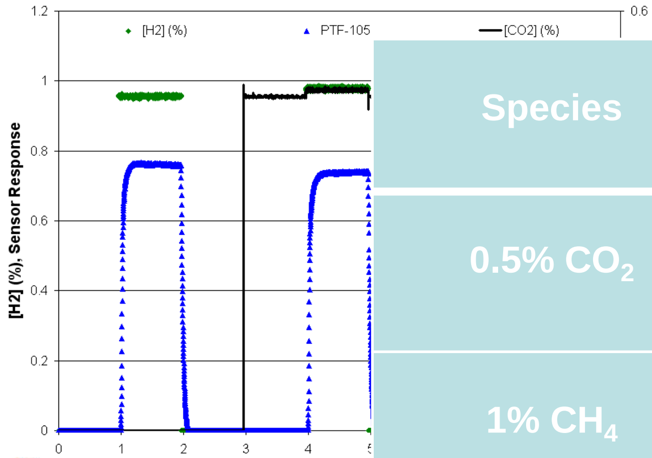
$K_{CO2} < K_{air} \rightarrow X_0 < 0$

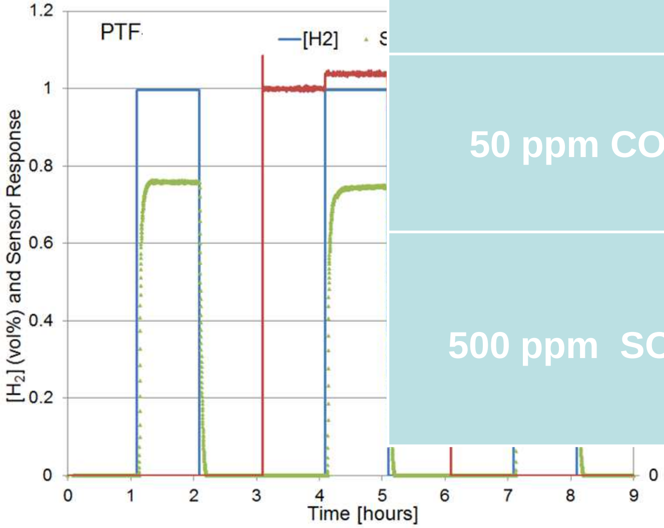
Species	X_0	X_H
1% CH_4	0.14 ± 0.02	-0.01 ± 0.02
0.5% CO_2	**-0.03 ± 0.02**	-0.00 ± 0.05

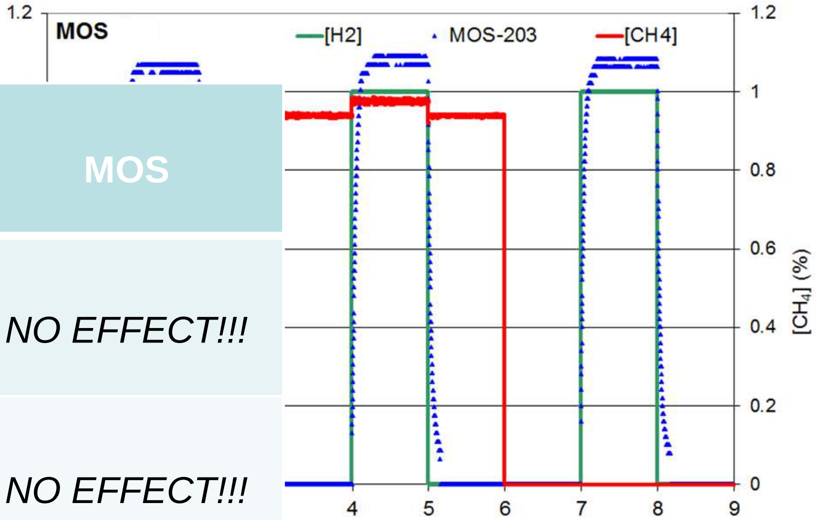


TCD response during the exposure profile with 1.0 vol% methane

Expensive platforms: PTF, MOS







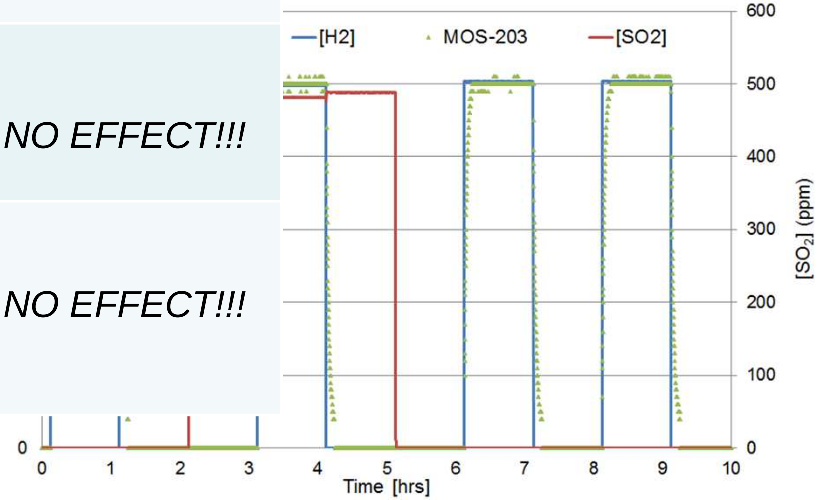


Table of results

Species	PTF	MOS
0.5% CO_2	*NO EFFECT!!!*	*NO EFFECT!!!*
1% CH_4	*NO EFFECT!!!*	*NO EFFECT!!!*
50 ppm CO	*NO EFFECT!!!*	*NO EFFECT!!!*
500 ppm SO_2	*NO EFFECT!!!*	*NO EFFECT!!!*

Summary of results

Species	PTF	MOS	EC	TCD	MOX	CAT
0.5% CO_2	NO EFFECT	NO EFFECT	NO EFFECT	Interferent	NO EFFECT	To be tested
1% CH_4	NO EFFECT	NO EFFECT	NO EFFECT	Interferent	Interferent	Interferent
50 ppm CO	NO EFFECT	NO EFFECT	NO EFFECT	NO EFFECT	NO EFFECT	NO EFFECT
50 ppm SO_2	NO EFFECT	NO EFFECT	Interferent POISON	NO EFFECT	To be tested	Interferent POISON

Conclusions and outlook

Expensive technologies (MOSFET, PTF) shows high selectivity to H_2 no poison effects, i.e. the sensors are well protected.

EC is poisoned by SO_2.

TCD shows cross sensitivity to CO_2 and to CH_4. No poison effect found.

Inexpensive technologies (CAT, MOX) shows high cross sensitivity to CH_4 and poison effects (SO_2), i.e. the sensors are not specific to H_2.

The effect of other gas species to be considered:

NH_3; NO_2; (N-based compounds)	H_2S (S-based compounds)	HMDS (Si-based compounds)

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Aknowledgements

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THANK YOU!!!

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H2Sense Workshop

H_2 Sensors – the right one in the right place at the right price

12th September 2013

Fuel Cell and Hydrogen Joint Undertaking, Avenue Toison d'Or 56-60, B1049 Brussels (4th floor)

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Extra slide: TCD

proportional

$$R_i \sim c_i \cdot (K_i - K_{Air}) + K_{Air}$$

$$R_0 \sim K_{Air}; c_H = 1\%$$

$$X_0^i = \frac{R_i - R_0}{R_H - R_0} = \frac{c_i}{c_H} \cdot \frac{K_i - K_{Air}}{K_{H_2} - K_{Air}} =$$

$$= \begin{array}{l} 0.5\% CO_2 : 0.5 \cdot \frac{0.64 - 1}{7.13 - 1} = -0.03 \\ 1\% CH_4 : \frac{1.30 - 1}{7.13 - 1} = 0.05 \end{array}$$

Gas Species	Thermal Conductivity K [mW/(m.K)]	K / K_{Air}
Air	26.2	1.00
Hydrogen, H_2	186.9	7.13
Helium, He	156.7	5.98
Carbon Dioxide, CO_2	16.8	0.64
Methane, CH_4	34.1	1.30
Carbon Monoxide, CO	25.0	0.95

Thermal conductivity of various gas species "i".

Experimental X_0 (0.5% CO_2)	Experimental X_0 (1% CH_4)
-0.03 ± 0.02 (agreement with calculations)	0.14 ± 0.02 (3 times the expected value)

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EC platform vs. SO_2

Net response to the interferent?

$$X_0^i = \frac{R_i - R_0}{R_H - R_0} = 0.06$$

Influence the sensitivity to H_2?

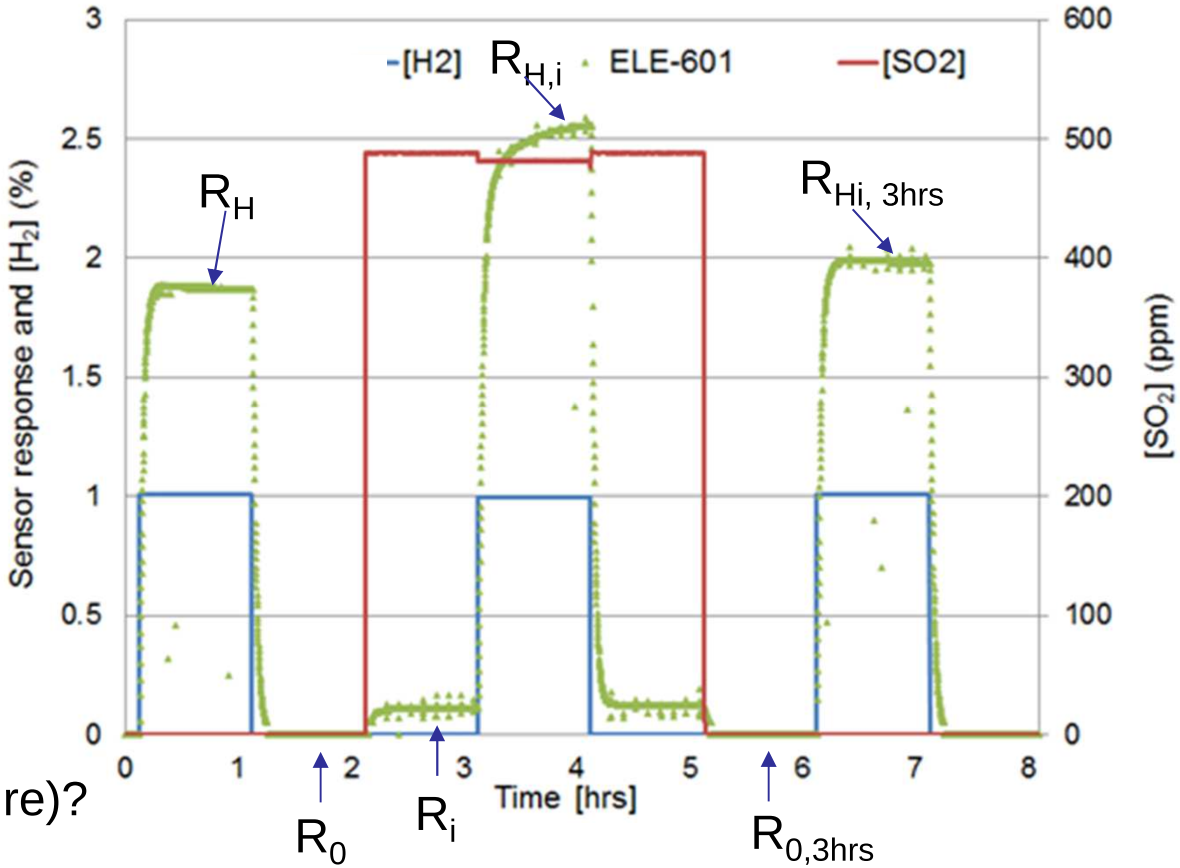
$$X_H^i = \frac{R_{H,i} - R_i}{R_H - R_0} - 1 = 0.30$$

Does it recovers (3h exposure)?

$$P_0^i = \frac{R_{0,3hrs} - R_0}{R_H - R_0} = 0$$

Sensitivity to H_2 (after 3h exposure)?

$$P_H^i = \frac{R_{H,3hrs} - R_0}{R_H - R_0} - 1 = 0.06$$



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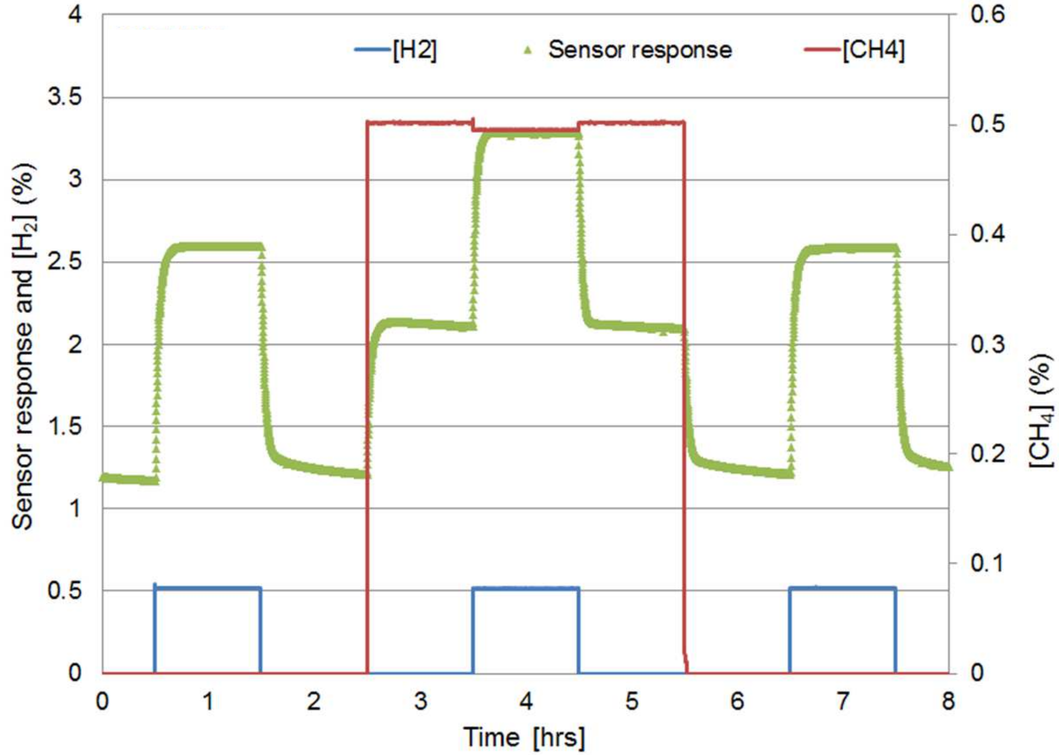
CAT platform

Negligible effect of CO and CO_2

Cross sensitive to CH_4: promoter for the absolute response; inhibitor for the net response.

Not a poison.

Species	X_0	X_H
1% CH_4	**0.66 ± 0.02**	**-0.18 ± 0.02**



CAT response during the exposure profile with 0.5 vol% methane.