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# Evaluation of selectivity of commercial hydrogen sensors

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ABSTRACT

The development of reliable hydrogen sensors is crucial for the safe use of hydrogen. One of the main concerns of end users is sensor reliability in the presence of species other than the target gas, which can lead to false alarms or undetected harmful situations. To assess the selectivity of commercial-off-the-shelf hydrogen sensors, a number of sensors of different technology types were exposed to various interferent gas species. Cross-sensitivity tests were performed in accordance with the recommendations of ISO 26142:2010, using the hydrogen sensor testing facilities of the National Renewable Energy Laboratory and the Joint Research Centre – Institute for Energy and Transport. Most of the sensor platform tested are unaffected by the exposure to the interferents. The metal-oxide and the thermal conductivity platform show a remarkable sensitivity to $CH_4$. None of the platforms tested were permanently affected by the exposure to the cross-sensitive species.


## Introduction

The European Commission and the U.S. Department of Energy (DOE) both recognise the key role hydrogen technologies will play in securing a safe, clean and secure energy supply in the future. In Europe, the *2011 Technologies Map of the Strategic Energy Technology Plan* identifies hydrogen and fuel cells as promising low-carbon energy technologies [1], which can assist in Europe's transition to a low-carbon society. Similarly, the Fuel Cell Technologies Office of the DOE supports the development and deployment of hydrogen as an alternative energy source [2] to ensure America's security and prosperity by addressing its energy, environmental, and nuclear challenges through transformative science and technology solutions [3]. Acknowledging the importance of safety in the future hydrogen infrastructure and the role hydrogen sensors play to help ensure this safety, sensor test facilities were independently established by the European Commission's Joint Research Centre Institute for Energy and Transport [4] and by DOE at the National Renewable Energy Laboratory (NREL) [5].

Hydrogen sensors are necessary for alerting to unwanted releases wherever hydrogen is produced, stored, transported, or used. Hydrogen sensors can employ one or more sensing

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technologies to detect and quantify hydrogen concentration. Many of these technologies are well developed and widely implemented in industrial applications [6]; however, the deployment of hydrogen safety sensors in new markets may impose new performance requirements. These include a need for increased robustness to ambient parameter changes and reduced cross-sensitivity to other gases. Stakeholders in emerging markets may be less knowledgeable about limitations associated with the various sensor platforms than their counterparts in established hydrogen industries, and thus may select a less-than-optimal technology for their application.

Cross-sensitivity, also called sensor selectivity, and robustness against potential "poisons" are some of the main challenges to the developers of gas sensors. Selectivity can be defined as the relative response of a sensor to two different analytes. Ideally, a gas sensor developed for a specific target analyte (e.g., hydrogen) should not respond to other gases (i.e., interferents). Selectivity reflects the ability of a sensor to respond to the target analyte regardless of the presence of other species. When the presence of a gas other than the target affects the sensor performance in a reversible way, it is termed an *interferent*, while species that affect sensor performance irreversibly are termed *poisons*.

Hydrogen facility designers and operators are concerned about the selectivity of their chosen hydrogen detection device. This concern was clearly evidenced during a NREL/DOE Hydrogen Sensor Workshop in 2011 when sensor selectivity was repeatedly cited by end users as a highly important analytical parameter of hydrogen sensors [7]. The response of a sensor to an interferent can lead to false positives. Such incidents of false positive alarms and their consequences have been reported [8]. Conversely, interferents may also suppress the sensor's response, leading to a false negative, which may have serious safety consequences as leaked hydrogen may go undetected.

For hydrogen sensors, a specific species may be a significant interferent on one sensor platform (e.g., methane on a hydrogen metal-oxide gas sensor) while it may not induce a response on a second platform (e.g., methane on a hydrogen electrochemical sensor). In this paper, we report the selectivity of various commercially available hydrogen sensor platforms. Although the number of commercially available hydrogen sensors is very large, most are based on a few sensing technologies or platforms [9], the main ones being electrochemical (EC) sensors, catalytic (CAT) pellistor sensors, metal-oxide (MOX) sensors, thermal conductivity (TCD) sensors, metal oxide semiconductor (MOS) sensors, and devices based upon palladium thin films (PTF). The cross-sensitivity of several of these platforms to potential interferent species, including carbon dioxide, methane, and carbon monoxide, was evaluated. These interferent species were chosen because of their interest to end users and because some have been listed as gases to which the cross-sensitivity of hydrogen detection apparatus shall be evaluated in the ISO standard on hydrogen detection devices [10]. This standard also lists a number of species that can potentially act as poisons for hydrogen sensors, e.g., sulphur dioxide, hydrogen sulphide, nitrogen dioxide, and hexamethyldisiloxane. The effect of these species on the performance of the selected hydrogen sensors is currently being evaluated and will be reported separately.

## Experimental

### Sensor selection

The cross-sensitivity to carbon dioxide, methane, and carbon monoxide was evaluated for five detection platforms. A representative commercial sensor of each platform type was selected, and cross-sensitivity tests were performed on these products. The technologies tested are listed in Table 1. Detailed descriptions of the detection principle of these and other hydrogen detection platforms are available elsewhere in the literature [11–15]. The sensor products were selected based on their proven robust performance, high level of development, and widespread deployment.

Various strategies are adopted to ensure sensor selectivity. Sensors based on chemical principles (e.g., PTF, EC, MOX) makes use of hydrogen-specific catalysts (e.g., palladium, platinum) and protective membranes against poisons. Numerous design strategies have been employed to minimise sensor cross-sensitivity [16], including adjusting the MOX crystal structure and composition with dopants, optimising the sensing material operating temperature for hydrogen detection, and covering the metal-oxide surface with a silica layer, which hinders the interaction of the metal-oxide with interferents. Being based on a physical interaction, TCD sensors are usually resistant to poisons but have some cross-sensitivity to species whose thermal conductivity differs significantly from air.

### Sensor testing

The impact of chemical interferents on commercial hydrogen sensors was evaluated using the hydrogen sensor testing facilities at the DOE's NREL in Golden, Colorado, and at the Joint Research Centre Institute for Energy and Transport in Petten, The Netherlands. Both facilities have been described previously [4,17]. Test conditions were maintained at 25 °C ± 2 °C and 100 kPa ± 10 kPa. Dry test gases obtained from gas cylinders were used in the evaluations so that the relative humidity was typically less than 5%. The gas flow in the chambers was set to 1000 sccm.

The desired test gas mixtures were generated by dynamic mixing of synthetic air, 2 vol% hydrogen in air, and certified mixtures of the interferent gas in air. The exposure profile used for the cross-sensitivity test is illustrated in Fig. 1 and consists of the following stages:

**Table 1 – Hydrogen sensor platforms evaluated for cross-sensitivity.**

| Sensor technology | Acronym |
|---|---|
| Metal oxide | MOX |
| Palladium thin film | PTF |
| Thermal conductivity | TCD |
| Electrochemical | EC |
| Metal oxide semiconductor | MOS |

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