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Advancements in Chemical-Gas Species-Specific Point-Sensors

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Abstract

Gaseous Chemical detection at trace levels is important to the space industry both for the safety of ground support equipment and space faring vessels. Gaseous point sensors are mature enough that inexpensive, small, and robust devices perform comparably to their bulkier, intricately complex, high-maintenance mass spectrometer counterparts. In particular, we will present an overview of technology for hydrogen and oxygen point sensors and display data for sensors of current technologies that represent today's state of the art point sensors. In the light of this technology, new developments and direction for the future of point sensor devices will be discussed. Hydrogen and oxygen sensor technology may carry over to other gas species with minimal effort and cost. We will also demonstrate how gaseous point-sensor technologies may be applied as novel solutions to future space applications as well as to modern industrial needs.

Introduction

Fuels for space vessels are typically toxic, and (obviously) explosive. Gaseous Chemical detection at trace levels is important to the space industry both for the safety of ground support equipment and space faring vessels. Trace gas detection ensures the absence of fuels or, upon detection, assists in leak location. The canonical method for trace gas detection is the mass spectrometer. These instruments utilize a combination of electric and magnetic fields to separate out ions with differing masses and then measure their concentrations with respect to the total pressure of the sample, i.e. it measure the partial pressures of the constituents of the gasses.

Although mass spectrometers are the workhorse of the industry, they have many drawbacks: they are bulky, they are somewhat delicate, they require frequent calibration, and they require expertise to operate. Kennedy Space Center uses mass spectrometers to monitor various gas concentrations including oxygen and hydrogen inside the aft compartment of the Shuttle. There are specific Launch Commit Criteria that limit the concentrations of these explosive chemicals in the aft.[1] The instruments require in-depth training to operate and the readings of the instrument are not always straightforward. In fact the LCC documentation, NASA document NSTS 16007 (HAZ-05) states: "The HGDSs are complex analytical instruments requiring expert operator interpretation of the data. Do not automate these measurements."[1] As a specific example, take the case of STS-93, where an unclear interpretation of mass spectrometer caused an unnecessary scrub at T-6 seconds.[2]

There exist means for detection of hazardous gases other than mass spectrometers. The category of interest for the purposes of this paper are those that transduce the presence of a chemical into an electrical signal. This paper will demonstrate that these point gas sensors can perform comparably to mass spectrometers and, in some instances, perform more favorably than mass spectrometers. All the while, they are very simple to operate, require very infrequent calibration, and detect a single gas with minimal cross gas sensitivity.
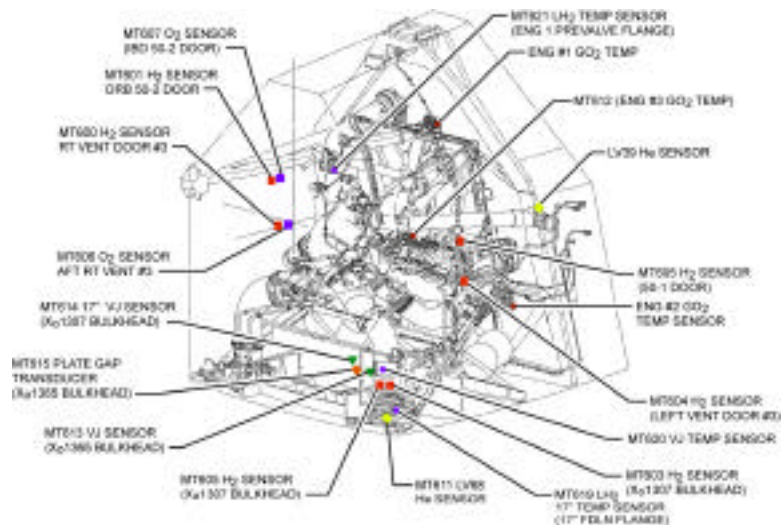

Figure 1 IVHM sensor positions.

IVHM Sensors

The Integrated Vehicle Health Management (IVHM) project HEDS Technology Demonstrator (HTD) called for placing hydrogen and oxygen sensors in the aft compartment of the Shuttle Orbiter to monitor gas levels before and during launch on the Space Shuttle Discovery. The placement of the IVHM sensors in the aft compartment are shown in Figure 1. The measurements of the gas sensors were to be compared to existing mass spectrometers for data before launch and to the results of catch bottles during launch. The catch bottles are "one-shot" pyrotechnic driven containers that enclose a trapped volume of gas at specific times during the mission. After landing, the trapped gases in the bottles are analyzed with a mass spectrometer to determine snap shots of gas concentrations in the aft throughout the mission. The role of the hydrogen and oxygen sensors in the IVHM experiment was to demonstrate that real time hazardous gas measurement are possible with point sensors both pre-launch and during flight.

## *Micro-Fuel Cell O$_2$ Sensor (Teledyne Analytical Instruments)*

The active elements chosen for the IVHM project oxygen sensors were manufactured by Teledyne Analytical Instruments (PN C43981-R21A). These elements were enclosed in an appropriate housing, ruggedized for flight, and the raw outputs were appropriately signal conditioned. To eliminate the possibility of temperature dependence of the sensor, the temperature of the entire assembly was held constant using an embedded thermometer/heater and controlled remotely in the IVHM electronics chassis. For further information on how the oxygen sensors were tested and the environmental conditions of the flight see IVHM document CTP-IVH-27-0362.

The Micro-Fuel Cell Oxygen Sensor is similar to a "battery" but differs in that the chemical reactants to create the electricity are totally or partially externally supplied.[3] The oxygen sensor contains an anode (lead) and a cathode (inert metal) with electrolyte surrounding them. In the case of this cell, oxygen is externally supplied while the other reactant, lead, is internal.

The reaction that takes place at the cathode is:

$$4e^- + O_2 + 2H_2O\ ??\quad 4OH^- \tag{1}$$

While the second reaction at the anode is:

$$2Pb + 4OH^-\ ??\quad 2PbO + 2H_2O + 4e^- \tag{2}$$
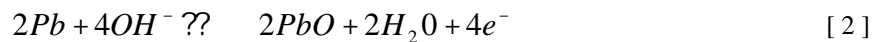
Summing the half reactions, [1] and [2], yields the complete reaction:

$$O_2 + 2Pb\ ??\quad 2PbO \tag{3}$$

One can see that the net reaction is the transfer of electrons from the Anode to the Cathode—a net current—and the subsequent oxidation of the lead into lead oxide. As is the case for a battery, there is a finite lifetime of the oxygen sensor. Once all the lead is oxidized to lead oxide, the cell no longer functions.
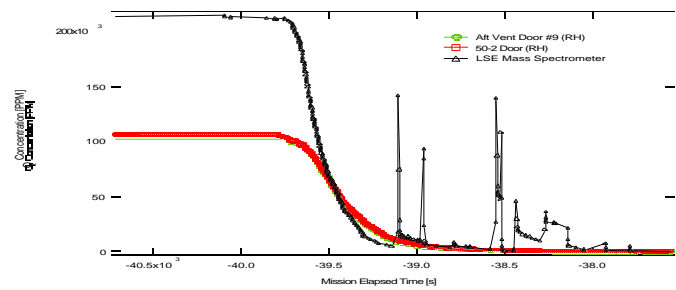

Figure 2 Pre-launch oxygen concentration in aft of STS-95. The green circles and red boxes are the two oxygen Points sensor data. The black triangles are the mass spectrometer data. (The flat region of the point sensors when T<-38x10^3 s is the upper limit for those sensors.)

After integration with the Shuttle Discovery and the IVHM data acquisition system, two of these sensors flew on STS-95 and STS-96. In Figure 2, some of the pre-launch data are displayed. The large drop in oxygen concentration around Launch-39.5x10^3 seconds is the purge of the aft compartment with nitrogen; hence the concentration drops to almost zero. As is evident in Figure 2, there is a good correlation between the mass spectrometer (black triangles) and the two oxygen sensors (green circles and red boxes). The discrepancy is presumably due to the difference in physical location between the devices. This is corroborated by the "jumps" in the mass spectrometer data, which correspond to position changes of the device pickup to various parts of the aft (with different response time at each position). The second pickup position of the mass spectrometer, around Launch-

39.1×10^3 seconds, is very closely located to the two oxygen sensors.

Although, the data in Figure 2 are somewhat redundant, the point sensors do allow real time simultaneous localization of oxygen concentration at different locations in the aft; data that would be extremely valuable in leak location. Where the point sensors provide novel data is during ascent. Figure 3 shows the continuous development of oxygen concentration throughout the ascent as measured by the point sensors as well as data collected from catch bottles. Even though the measurements do agree after T+100 seconds, the large disagreement between the catch bottle and the point sensors before T+100 seconds is undetermined. This T<100 second discrepancy is most likely a result of the difference in physical location of the devices. One must remember that the atmosphere contains 20.93% volume, so some of this discrepancy may be due to atmosphere leaking into the aft (atmospheric origin of the oxygen can be determined using argon concentration).
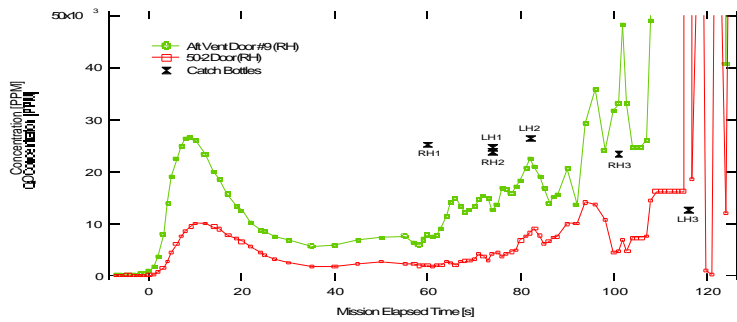

Figure 3 Oxygen Concentration on ascent. The green circles and red boxes are the oxygen sensors. The black hourglasses are results from catch bottles measured after landing. (The flat region of the point sensors when T>120 s is the upper limit for those sensors.)

In Figure 3 there is a noticeable feature around T+10 seconds that is not seen with the catch bottles. This peak in oxygen concentration is easily understood by the fact that after launch, the nitrogen pressurization of the aft is no longer present. Atmosphere creeps in locally around the sensors through the #9 vent doors(indicated by the rise in concentration), but when the shuttle starts accelerating, the rush of nitrogen from the payload bay and the upper part of the aft quickly purges through those vent doors causing the decrease in concentration again.

Platinum Based H$_2$ Sensors (Makel Engineering)

The sensor chosen for the IVHM project hydrogen sensors were manufactured through a collaborative effort with University, NASA, and Industry. The active elements were designed and fabricated jointly by Case Western Reserve University and NASA Glenn.[4] The sensor electronics, packaging, and signal condition were developed and commercialized by Makel Engineering. The KSC Transducer Development Lab worked very closely with Makel Engineering to adapt their product for flight and to integrate them into the IVHM data acquisition
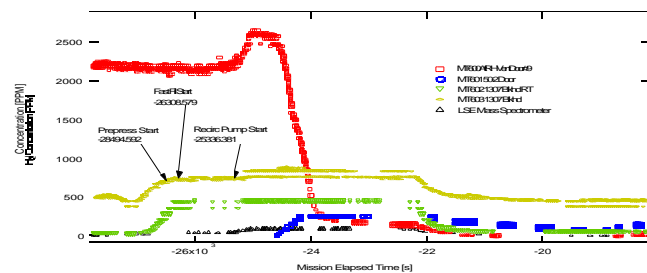

Figure 4 Aft H$_2$ Concentration for STS-95 before launch. The black open triangles are mass spectrometer measurements, all others are Makel Hydrogen point sensors.

system and the Shuttle Discovery. For further information on how the hydrogen sensors were tested and the environmental conditions of the flight see IVHM document CTP-IVH-26-0352.

The operation for the sensor element is based on hydrogen's peculiar adsorption properties onto Palladium (Pd). Hydrogen will, quite uniquely, adsorb and absorb onto palladium (See references for a review)[5]. As H$_2$ disassociates to H$^-$ and goes into solution, the Palladium lattice expands. Along with this expansion and many other phenomena, palladium's bulk electrical properties are affected. For steady state conditions, the concentration of hydrogen in palladium is directly related to the partial pressure of hydrogen. Therefore the electrical properties are an indirect measurement of the partial

3

pressure of hydrogen. On the Makel sensor, high concentrations (above 1000 PPM) are measured using a Palladium resistor. Low concentrations (below 1000 PPM) are measured using a Palladium-based Shotky diode. The Makel sensor uses a palladium-chromium alloy to avoid some other hydrogen-Palladium issues that are discussed elsewhere.[4, 6]

Figure 4 shows the results from STS-95 for some of the six Makel hydrogen sensors before launch along with the Ground Support Equipment mass spectrometer. There is considerable correlation between the mass spectrometer and the point hydrogen sensors. Again, the small discrepancies are most likely due to different physical locations in the aft. Note that the point sensors indicate some of the labeled events that are not

Figure 5 Aft H$_2$ Concentration for STS-95 during ascent. The black hourglasses are the catch bottles, the rest are the Makel point sensors.

evident in the mass spectrometer. As with the point oxygen sensors, simultaneous real-time measurement at multiple locations has many advantages for safety and leak visualization.

Figure 5 shows the data for the hydrogen sensors during ascent. There is a remarkable correlation between the catch bottle results and the point sensor data. One can see the entire development of hydrogen concentration in the aft. Locality discrepancy during ascent is a smaller effect with hydrogen because, unlike oxygen, the only leak source for hydrogen is the fuel lines (the atmosphere only contains 0.5 PPM of hydrogen on average).

Figure 6 shows perhaps some of the most interesting and never-seen-before data around Main Engine Cutoff and External Tank separation. There is a feature right around External Tank separation, where an effluvium of hydrogen can be seen to propagate through the aft. This is most likely a result of remnant gas escaping from and around the external tank umbilical. These data are only qualitative because no pressure data is available for T>+120 seconds that would allow us to calculate true concentrations.

Future Point Sensors
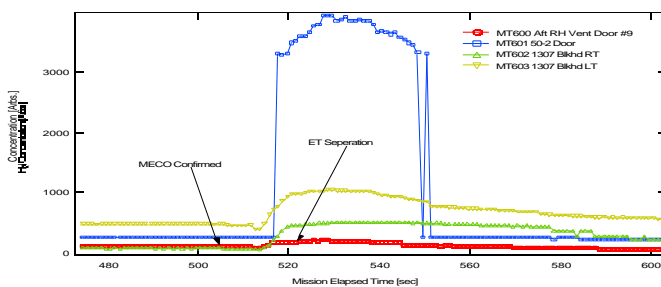
Zirconium O$_2$ Sensor

Figure 6 H$_2$ Concentration in aft during ascent. Note that this graph is after pressure data are available so that the concentration units are arbitrary.
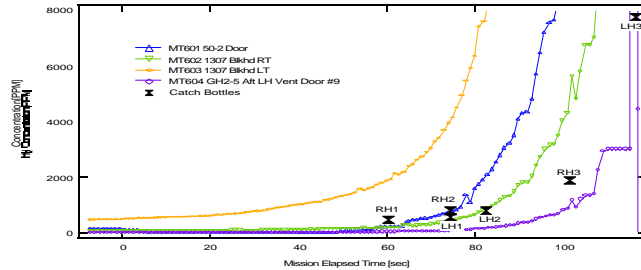
The oxygen sensors used for IVHM were Micro-Fuel cells with a finite lifetime. There is considerable interest to develop sensors for space applications that would not have this finite lifetime. The automotive industry has used oxygen sensors to regulate combustion in engines.[7] They have used the Micro-fuel cell, but a more attractive technology is the use of Zirconium Oxide. KSC has worked with two companies in development of the Zirconium Oxide technology for space applications, Electrovac and Makel Engineering.

The technology is based on the electrolytic properties of oxygen in Zirconium Oxide. The cell consists of Zirconium Oxide plated with Platinum electrodes on either side. At temperatures around 600 °C, O$_2$ dissociates on the

surface of Platinum into O^{-2} and can propagate through the solid Zirconium Oxide electrolyte. Conventional methods transduce this reaction potentiometrically by relying on a reference gas on one side (that is an infinite reservoir) and the sample on the other, separated by the electrolyte. Then one merely measures the voltage between each side, which is a direct measurement of the difference in chemical potential, or the partial pressure, between both sides. Note that during this measurement, oxygen moves back and forth from the sample gas and the reference gas; a potential problem if you have finite quantities of either. Also, this measurement has diminishing accuracy with increased difference from the reference (not typically good for measurements less that 1% or greater than 30%).

A better application for measurement of finite amounts of gas is to amperometrically measure the reaction. This method involves placing a cap with a small orifice on one side of the electrolyte, and, instead of measuring the voltage, a voltage is applied. The applied voltage will pump oxygen from one side of the electrolyte to the other. The oxygen flow/electrical current will be limited only by the geometrical constraints of the cap on the active side, and the limiting current given by:

$$I_{limiting} \quad \ln \frac{1}{1 - \frac{C_{oxygen}}{C_{total}}} \qquad [4]$$

will be a direct measure of the oxygen concentration. Where C_{oxygen} is the molar oxygen concentration and C_{total} is the total molar concentration of the gas. This measurement does not rely on a reference gas and has a much wider possible range of operation.

Electrovac currently supplies amperometric oxygen sensors that measure from 0-98%. One of the main development efforts is to extend this range to 100% for use in situations where knowledge of the purity of pure oxygen needed. One such application would be for In Situ Propellant Production on the surface of Mars. One should be sure that the oxygen produced is clean, so that a vessel could be safely and effectively fueled. KSC has, and will continue to work to reach this goal of a 0-100% oxygen point sensor.

Makel Engineering (once again, in conjunction with Glenn research center and Case Western Reserve University) has also developed a MEMS (Micro Eletro-Mechanical Systems) amperometric oxygen sensor and packaged it with their Palladium based hydrogen sensor.[8] Its targeted region of interest is less than 1%. One of the advantages of the Makel oxygen sensor is that due to it small size (microns) it consumes a very small amount of power to heat the ZrO_2 to 600 °C. KSC has been involved in the testing of this sensor and it shows great promise.

Quartz Crystal Microbalance H₂ Sensor

A development in hydrogen sensing in progress at KSC will exploit the adsorptive properties of hydrogen in palladium, but instead of attempting to measure the electrical properties of the palladium (to deduce hydrogen concentration), we propose to measure the adsorbed hydrogen mass gain directly. The most straightforward way to do this is with a quartz crystal microbalance (QCM) coated with a palladium-chromium alloy. For a review of QCM's see References.[9]

For crystals with certain broken symmetries, application of an electric field causes the crystal to "deform". This deformation is known as the piezoelectric effect. The most widely used piezoelectric material is quartz, used ubiquitously as a time standard. Placing a quartz crystal in the appropriate circuit causes it to behave like an oscillator both mechanically and electrically. Like any simple harmonic oscillator, the frequency of oscillation of the quartz crystal is proportional to the amount of mass attached to its face (for small additions of mass). This oscillation can be used as a very sensitive "inertial" balance. There have been many complex analyses for addition of large masses to quartz oscillators, but Saurbrey[10] (1959) and later extended by Behrndht[11] (1971) and Denison[12] (1973) showed that the frequency shift for small mass additions is linearly proportional to the change of the period of vibration by the following formula:

$$M_q = \frac{_q v_q}{2} \left(\frac{1}{f_c} - \frac{1}{f_q} \right) \qquad [5]$$

where m_q is the mass of hydrogen adsorbed, $_q$ is the density of the quartz, v_q is the shear wave velocity, f_c is the frequency of the crystal with the adsorbent, and f_q is the initial frequency of the crystal. Rearranging this equation in the following form:

$$M_q = -(f_c - f_q) \frac{_q v_q}{2 f_c f_q} \qquad [6]$$

Then taking the final term, one can see that if f_c f_q then the sensitivity goes as f_q^2. There is a large gain in sensitivity for increasing frequency of the oscillator.

The idea behind the QCM for gas sensing is to measure mass gained by a gas adsorbing to the surface of the oscillator. Although others have made attempts at developing a QCM based hydrogen sensor by coating the surface with a hydrogen adsorbent, none have combined the correct ingredients to make a successful product (for a review see References[5]). We propose, through proprietary methods, to combine those correct ingredients to produce a device that would be capable of measuring in the 10 PPB range.

Conclusion

Both the hydrogen and oxygen IVHM sensors performed well. Both sets of sensors survived two launches safely. (The launch data from the second mission is not presented here for brevity's sake). Not only did they each correlate with mass spectrometer measurements currently used with the Space Shuttle, they went further to provide data where none were previously available. Future work would be necessary to confirm the quantitative behavior of the sensors during launch.

The development of future point sensors at KSC will serve to expand the capabilities and extend the range of current point sensors. Not only will these sensors serve the space industry, but they may carry over to industry. With the advent of the Fuel-Cell, future automobiles may have need for small reliable hydrogen detectors. The power industry also has need for hydrogen detectors around transformers to detect breakdown in the hydrocarbon electrolytes, which the Quartz Crystal Microbalance technology may be readily applied. The QCM technology may also very easily transfer over to other gas species merely by substituting the palladium coating with another that is sensitive to that gas species. Point sensors are now mature enough to where they may now serve as an adequate replacement for Mass Spectrometers in many applications and in some applications outperform them. With future development, there may even be multiple point sensors on a single chip that would act as a Mass Spectrometer on a chip.

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