

FINAL PROJECT REPORT**WTFRC Project Number: # 2005-10****Project Title:** Ethylene Measurement in Post-Harvest Storage**PI:** Reza Shekarriz, Ph.D.**Organization:** Fluid Analytics, Inc.**Telephone/email:** 503-234-2747, x110**Address:** 3525 S.E. 17th Ave.**Address 2:****City:** Portland**State/Province/Zip:** OR, 97202**Co-PI(2):** Dr. Lloyd Allen**Organization:** Fluid Analytics, Inc.**Telephone/email:** 503-234-2747, x106**Address:** 3525 S.E. 17th Ave.**Address 2:****City:** Portland**State/Province/Zip:** OR, 97202**Budget History:**

Item	Year 1:	Year 2:	Year 3:
Salaries	25000	16000	
Benefits	10000	6400	
Wages	8900	6120	
Benefits			
Equipment	3000	1500	
Supplies	1000	2000	
Travel	500	1500	
Miscellaneous	3738	2570	
Total	57138	39290	

I. PROJECT OBJECTIVES

I.1. Year 1: 0.1 ppm Ethylene Sensor Development and Demonstration

- 1) *Design and fabricate prototypes for near real-time ethylene testing at 0.1 ppm and higher, with simple operation and maintenance.* This system will be designed in a modular fashion such that manufacturing, assembly, and component replacement for maintenance are rendered very efficient.
- 2) *Test and evaluate performance of prototype in laboratory and field.* The critical parameters to be evaluated are sensitivity, selectivity, accuracy, and stability. We will use the results as a basis for production engineering and commercialization of a hand-held package, which would include all the required cost and performance attributes necessary for the apple post harvest market.

I.2. Year 2: Low Cost Miniaturized Prototype Development and Demonstration

Design, fabricate, and field test a miniaturized and low cost version of the prototype for near real-time ethylene testing at 0.1 ppm levels.

II. SIGNIFICANT FINDINGS

Several major accomplishments are highlighted below and further discussions of the results will follow in the upcoming sections.

1. *High sensitivity near real-time ethylene detection:* During the course of this study our electrochemical sensor demonstrated typical sensitivity of approximately 100-ppb. By careful fabrication of the sensor cell 10-ppb sensitivity could be realized for ethylene in air or pure nitrogen backgrounds, representing RA and CA rooms, respectively.
2. *Miniaturization and packaging of the system:* The entire sensor cell, the fluidic system for sampling the air, the data interpretation electronics system that comprised of two circuit boards and power module all fit inside a field-portable compact sensor unit.
3. *Alpha prototype development and field demonstration:* A battery-operated alpha prototype was completely engineered, manufactured, assembled, and tested in the laboratory and in the field. The utility of this system was demonstrated for measurement of the amount of ethylene produced by a single apple and for a variety of apples, even for those producing very little ethylene.
4. *Low cost ethylene sensor development:* Depending on the specific sensing options and built-in functionalities of the system, the projected price is below \$5,000 and may be as low as \$2,000. Given the capabilities of the system, this provides a very competitive product and one that offers a cost effective and higher throughput sampling and monitoring option for determining maturity of fruit in the harvest and post-harvest phases.

III. METHODS: ELECTROCHEMICAL SENSING OF ETHYLENE

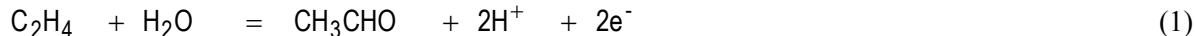
As a fruit ripening hormone, ethylene gas is effective at greater than 0.1 ppm; one part of ethylene per million parts of air represents one cupful of ethylene gas in 62,000 gallons of air – not much.¹ Constant ethylene monitoring is essential because automotive emissions, plastics, smoke and

¹ California Fresh Market Advisory Board, Informational Bulletin No.12, June 1, 1976.

fluorescent lights all increase ethylene gas levels.²⁻³ A single propane-powered forklift can cause serious damage in highly ethylene gas-sensitive commodities. Ethylene will permeate through produce cardboard shipping boxes, wood, and even concrete walls.⁴

The current approach for post-harvest ethylene sensing is based on the electrochemical oxidation of ethylene as described above. The oxidation of ethylene at a gold anode in an electrochemical cell provides a cell current that can be measured and used for the determination of ethylene in air. This electrochemical process is interestingly similar to the ozone oxidation of ethylene that produces a chemiluminescence signal that is used in one of the ethylene sensors discussed below. The oxidation of ethylene by ozone is driven by the chemical energy resident in the ozone. The driving force for electrochemical oxidation of ethylene in the cell is the electrical cell potential and the pH of the electrolyte. Since oxidation of ethylene is common to both processes, the selectivity of both processes is very similar. The important difference is that the electrochemical process requires neither an ozone generator nor a photodiode for converting chemiluminescence photons to electrical current. Compared to chemiluminescence, the electrochemical process is not only simpler in terms of hardware required but it is much more amenable to miniaturization and mass production. Therefore, we believe the electrochemical process using the gold anode as the technology base can provide a new generation of ethylene sensors that have high sensitivity and are low in manufacturing cost.

Interestingly, research on the process and application of the oxidation of ethylene at a gold electrode has been reported in the scientific literature during the past decade. The chemistry of the oxidation of ethylene on gold was studied and reported by Volkmar Schmidt.^{5,6} They reported that an electrolytic cell using porous surface gold with 0.05 M H₂SO₄ electrolyte produced a maximum cell current just below 1.3-V in the presence of ethylene. Products for both partial oxidation of ethylene to acetaldehyde and for full oxidation to CO₂ were detected through mass spectral analysis of cell off gases.



Ethylene was isotopically enriched with deuterium in order to determine the difference between acetaldehyde and CO₂, which both have a normal mass of 44 amu. They speculated that the first step in the process is the complexation of ethylene to the gold surface through the π -bond in ethylene. The researchers concluded "Gold in acid solution can in principle be regarded as a selective electrocatalyst for the oxidation of unsaturated hydrocarbons as well as unsaturated alcohols (Schmidt and Pastor, 1994)." In their testing, Schmidt and Pastor bubbled ethylene into the cell electrolyte directly. Shortly thereafter, Peter Hauser reported using a layer of gold plated onto a Nafion membrane as the anode in an electrochemical cell for determining ethylene and other oxidizable molecules present in air.^{7,8} Professor Hauser utilized Nafion as a Solid Polymer Electrolyte (SPE) in the cell such that it provided a partition between the gas side of the cell and the liquid electrolyte. When gas was passed over the gold, ethylene in the air was catalytically oxidized. Hauser's cell bears a significant resemblance to the electrodes and SPE in a PEM fuel cell. The difference is that the SPE in a fuel cell provides the partition between two gas chambers. Hauser reported that cell response to

² Ethylene Control, Inc. "About Ethylene Gas" (taken from independent study in 1997 at the University of California Davis). Retrieved from WWW Aug. 18, 2004 www.onsolution.com.au/EthyleneControl/about.html.

³ California Fresh Market Advisory Board, Informational Bulletin No.12, June 1, 1976.

⁴ California Fresh Market Advisory Board, Informational Bulletin No.12, June 1, 1976.

⁵ Schmidt, V.M., and E. Pastor, 1994, Adsorption and oxidation of acetylene and ethylene on gold electrodes." *Journal of the Electrochemical Society*, 376, pp. 65-72.

⁶ Pastor, E, and V.M. Schmidt, 1995, "Electrochemical Reactions of Ethene on Polycrystalline Au Electrodes in Acid Solution by Differential Mass Spectrometry and Isotope Labeling", *Journal of Electroanalytical Chem.*, 383, 175-180.

⁷ Jordan, L.R. and P.C. Hauser, 1997 "Amperometric Sensor for Monitoring Ethylene", *Anal. Chem.* 69, 558-562.

⁸ Hodgson, A.W.E., P. Jacquinet, L.R. Jordan and P.C. Hauser, 1999 "Amperometric Gas Sensors with Detection Limits in the Low ppb Range." *Analytica Chimica Acta*, 393, 43-48.

ethylene was “linear at least up to 500 ppm.” He established that 40 ppb was the detection limit based on a signal-to-noise-ratio (SNR) of 3 in his measurement system.

It is clear that this method of amperometric gas analysis presents a novel and potentially practical approach as a basis for a commercial sensor business. For this to become reality, further research into electrode configuration, cell conversion efficiency, signal analysis and conditioning, cell engineering, and water and air flow management needed to be performed to achieve the desired sensor sensitivity, SNR, and reliability.

IV. RESULTS AND DISCUSSION

The current work plan covers tasks in areas that encompass the objectives component engineering, system integration, and performance evaluation testing.

IV.1. Task 1: Gold Electrode Design and Development

At the heart of our device is an especially developed nanoporous gold catalyst deposited on the surface of a Nafion[®] membrane using two different techniques. Although gold is considered to be a noble and extremely unreactive metal, numerous reports in recent years show that atomic gold clusters ranging in size from 2 to 20 nm are highly active as heterogeneous catalysts in a number of chemical reactions.^{9,10,11} Other typical catalytic metals such as platinum, palladium, nickel, cobalt and others have been shown to have interesting catalytic properties as nanoparticles, but these metals are already known heterogeneous catalysts.¹² Gold in a nanoparticulate state however, provides a new area of catalysis research, sometimes known as the “New Gold Rush.”

Typically, a heterogeneous catalyst consists of a small amount of metal deposited on the surface of a metal oxide. The metal oxide: alumina, ceria, ferric oxide, titanium dioxide or mixtures of metal oxides provides a support for the catalytic metal, and in oxidation reactions, provides a source/sink for oxygen in the reaction. To be a catalyst, the dispersed metal must first adsorb both reactants, and not attract the products significantly. This mechanism provides the pathway for bringing reactant molecules together to facilitate the reaction. Interestingly, nanoparticle gold on a number of metal oxide substrates has attracted much attention for the catalytic oxidation of many small molecule and carbon-containing compounds. This is an important property for our detection of small molecules of ethylene adsorbed to the nanoparticle gold (Figure 1).¹³ This makes them ideal targets for electrochemical oxidation using our nanoparticle gold

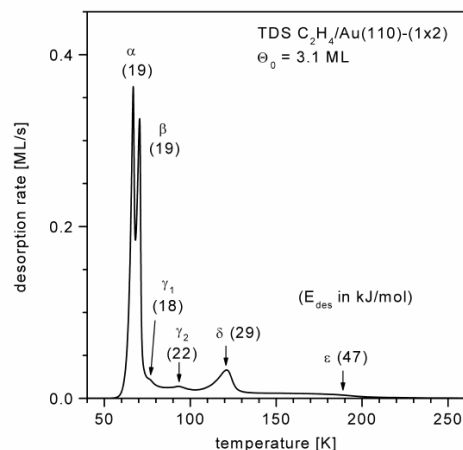


Figure 1. Thermal Desorption Spectroscopy (TDS) for adsorption of ethylene on gold (Gottfried, 2003).

⁹ Didier Astruc, Feng Lu, and Jaime Ruiz Aranzaes. Nanoparticles as recyclable catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angew. Chem. Int. Ed.* 2005, 44, 7852-7872.

¹⁰ .A. Sanchez, et al. When gold Is Not Noble: Nanoscale Gold Catalysts. *J. Phys. Chem. A* 1999, 103, 9573-9578.

¹¹ Cortie, M.B. and E. van der Lingen, 2002, “Catalytic Gold Nano-Particles,” *Materials Forum*, 26, pp. 1-14.

¹² Thompson, D., 1999, “New Advanced in Gold Catalysis – Part II,” *Gold Bulletin*, 32(1), pp. 12-19.

¹³ Gottfried, J. M., 2003, “CO Oxidation over Gold Adsorption and Reaction of Oxygen, Carbon Monoxide, and Carbon Dioxide on an Au(110)-(1×2) Surface,” Ph.D. Dissertation, fu Berlin, <http://www.diss.fu-berlin.de/2003/133/indexe.html>.

electrode cell operating at moderate cell potentials. The successful oxidation of ethylene, propylene, ethylene glycol, formaldehyde, formic acid and carbon monoxide with air or oxygen has been reported.¹⁴

The specifics of our deposition approach constitute some of our intellectual property for producing highly reliable and repeatable high surface area catalysts. Figure 1 shows a sample of our gold catalyst at different magnifications. Note that the top left image is a gold film with little to no porosity, appearing as a brilliant gold and highly reflective layer under the microscope. The right image labeled as 1X has the right appearance for a very effective gold catalyst and appears to have small lumps under a microscope with 200X magnification. The lower image is an image taken with SEM at 25,000X magnification, which shows the gold particles of smaller than 100-nm in diameter.

IV.2. Task 2: Prototype Design and Fabrication

In order to construct a handheld, easy to use prototype, a lot of design work had to occur. Factors that had to be considered in the design included ease of use, adaptability to different testing configurations and environments, chemical compatibility, size, rigid handling of plated membranes and catalyst surface area. After looking at each of these factors, the design was fabricated. A rendering of the design along with the finished product are shown below.

The test cell is small, measuring only 3.25 inches tall and approximately 2 inches wide with an additional 1.5 inches in width being due only to the mounting structure. The cell's inlet and outlet ports can be adapted to almost any pipe or compression fitting size, which will make it easy for testing different gas inlet configurations or environments. The catalyst exposed surface area is approximately 2.5 times larger than any previously tested surface area which rendered our cell response larger making smaller ethylene concentrations easier to detect. One of the biggest additions in this test cell that was not addressed in any previous version is the addition of a semi-rigid frame for the catalyst membrane. This provided a more robust construction and easier handling during assembly.

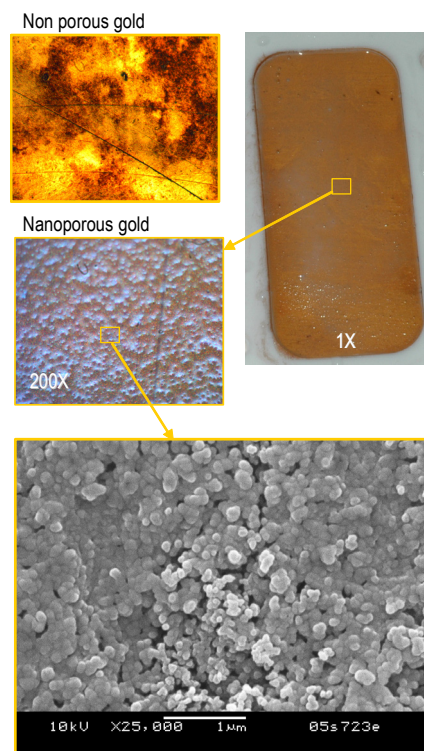


Figure 2. Nanoporous Gold Catalyst.

¹⁴ Burke, L.D. and P.F. Nugent, 1998, "The Electrochemistry of Gold: II The Electrocatalytic Behaviour of the Metal in Aqueous Media," *Gold Bulletin*, 31(2), pp. 39-50.

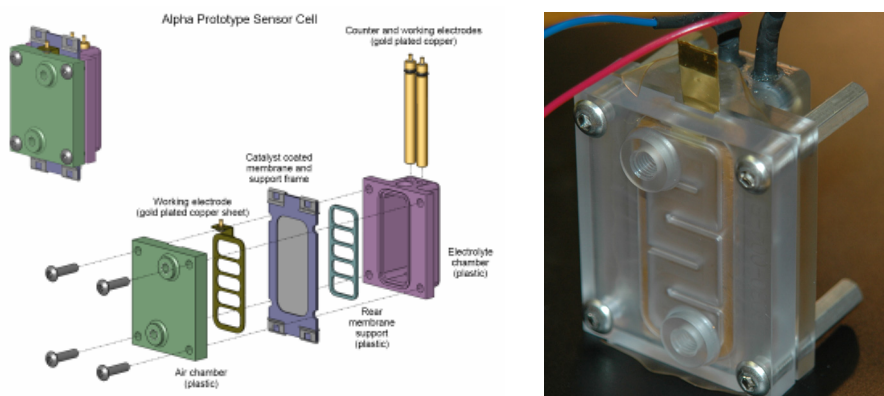


Figure 3. Electrochemical cell design for the alpha prototype .

The complete ethylene sensing instrument is packaged in an engineered sheet metal enclosure. The enclosure serves as a rugged framework for mounting the internal components, while providing an attractive and protective shell. Figure 4 shows the rendered CAD design of the box, and a photograph of the finished enclosure.



Figure 4. Photograph of complete alpha prototype.

IV.3. Task 3: Prototype Performance Testing and Evaluation

A new test apparatus was designed and built keeping many factors in mind. Some of the main factors considered when designing the new test apparatus include: (1) ensuring that the mixing of 10 ppb of ethylene in nitrogen is achievable with a higher level of confidence than was previously achievable; (2) designing such a system that the actual cell response would not be left in question due to inability to fully characterize the test system response time; (3) allowing for ease of use; and (4) minimizing overall test setup size. After careful consideration of these factors, a design was created that satisfied the needs.

Also incorporated into the new test apparatus is a Princeton Applied Research (PAR) potentiostat, model 263A-1 as well as three tanks of cylinder gas (10-ppm ethylene in nitrogen, 1-ppm ethylene in nitrogen, and 100% nitrogen). The potentiostat gives us in house capabilities to perform all testing without the need to travel to other laboratories. Step testing performed with membranes 0009 and higher was done using the complete prototype and the potentiostat boards as opposed to the PAR 263A-1 potentiostat.

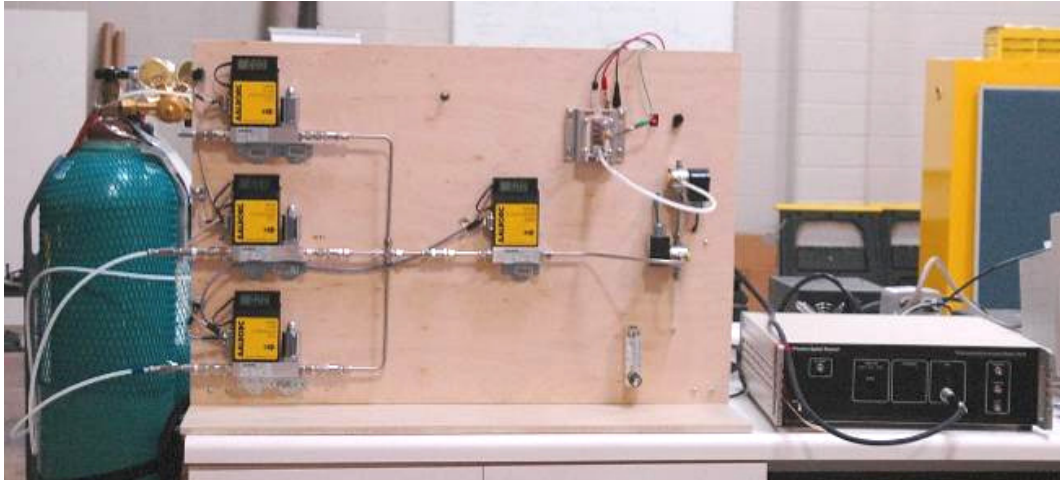


Figure 5. The final test apparatus incorporates all of the goals put forth and is currently fully functional.

Initial step tests consisted of keeping the operating voltage and flowrate constant and changing the ethylene concentration. The standard initial step test changes the concentration from 0 ppm to 5 ppm and from 0 ppm to 10 ppm. These concentration changes are easily seen and made a good quick evaluation point in order to compare performance between different membranes. Figure 6 shows step test results from membrane 0006. Membrane 0006 showed approximately 4 microamps per ppm response. As mentioned before, fabrication of the membrane has a tremendous impact on the sensitivity of the device. While membrane 0006 showed good sensitivity, we have results from electrodes that showed little to no sensitivity to ethylene because of variability in the plating process. The figure on the right shows the linear relationship between the ethylene sensitivity and ethylene concentration, showing sensitivity down to 10-ppb of ethylene.

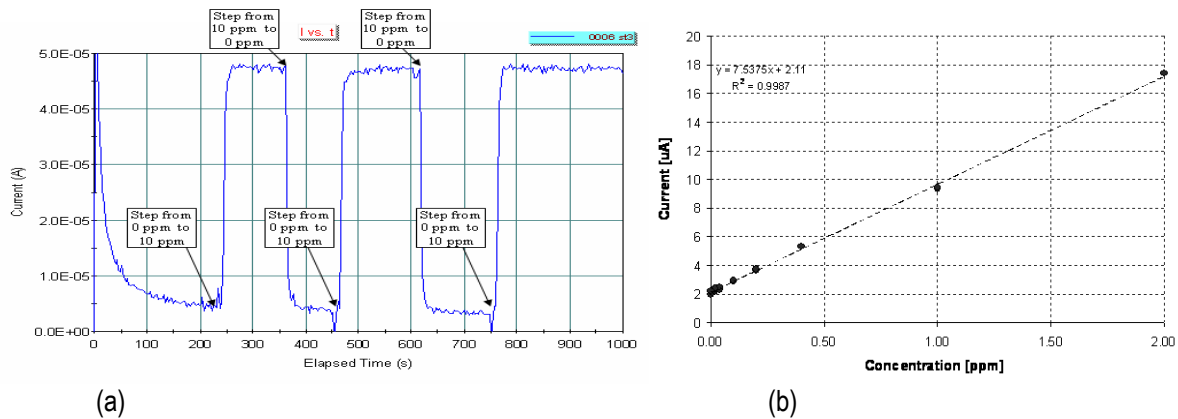


Figure 6. (a) Initial step test for membrane 0006; (b) Sensitivity versus concentration.

Because of the positive results achieved with membrane 0006, additional tests were performed on this membrane for a more inclusive characterization. The next tests performed on membrane 0006 were voltage tests. From a cyclic voltammogram we get a rough idea of the optimal operating voltage, but it does not tell us what happens if the voltage is shifted slightly. The shape of the response versus voltage curve is useful in determining the level of accuracy needed in our electronic voltage control, as well in determining the optimal voltage for sensing a particular species, in this case ethylene

molecules in air. Voltage tests consisted of first running the cell at 0.5 V (the baseline voltage for these tests), performing two sets of a 0 ppm to 10 ppm, longer than 200 s pulse, then changing voltage and repeating the concentration pulses. Flow rate was kept constant at 200 sccm for the entire test. The plot shown in Figure 7 represents the sensor response at different biased voltages maintained on the electrode. The sensor response at $\sim 0.5\text{V}$ and above (within the tested range) does not show a large dependence on the operating voltage. This is very useful information that was used in selecting suitable electronics.

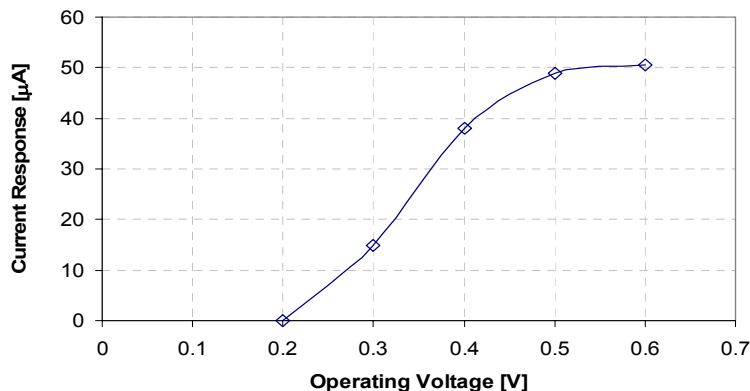


Figure 7. Operating voltage vs sensor response curve shows a plateau starting at $\sim 0.5\text{V}$

Figure 8 shows the results of pH variation vs sensitivity and offset. Sensitivity increases with decreasing pH (aka increasing acidity). In the highest pH solutions tested the system was not very stable and large fluctuations were observed. Testing is still in progress to evaluate the range of pH from 1 to 2.5. We are also planning tests to evaluate the impact of position and geometry of the counter electrode on cell electrical stability.

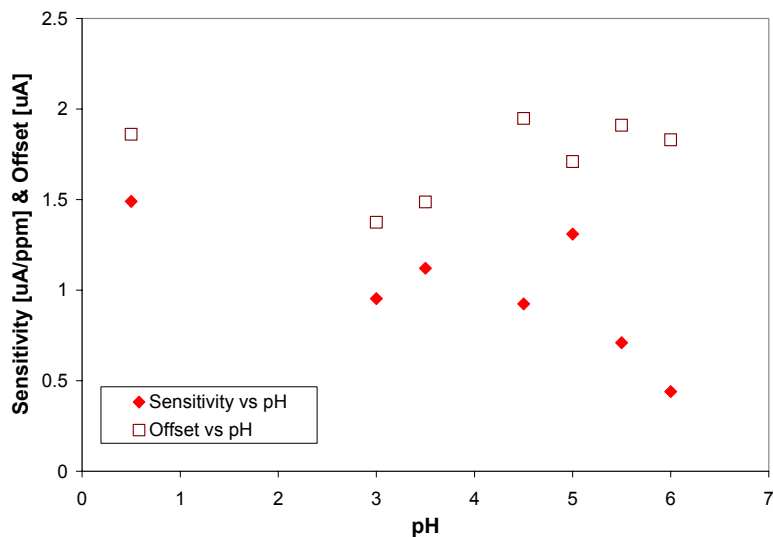


Figure 8. Sensor response vs pH.

Two factors that affect operation of the sensor under the cold storage environment are variation in the oxygen content in the air and changes in the temperature. The variation in sensor sensitivity as a function of temperature was determined using a set of tests in a controlled atmosphere chamber. The sensitivity of the sensor seems to be linearly correlated to temperature and increased with increasing

temperature as shown in Figure 9. Note that the sensitivity in cold storage temperature conditions is nearly half of what we would expect at room temperature. The tests in the standard room air condition versus nitrogen only environment shows slight increase in sensitivity with exposure to air or higher oxygen levels (Figure 10).

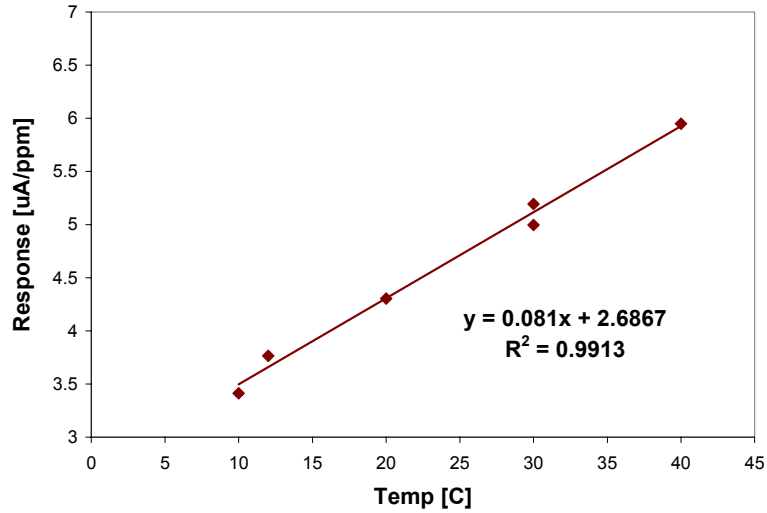


Figure 9. Sensitivity appears to increase with increasing temperature.

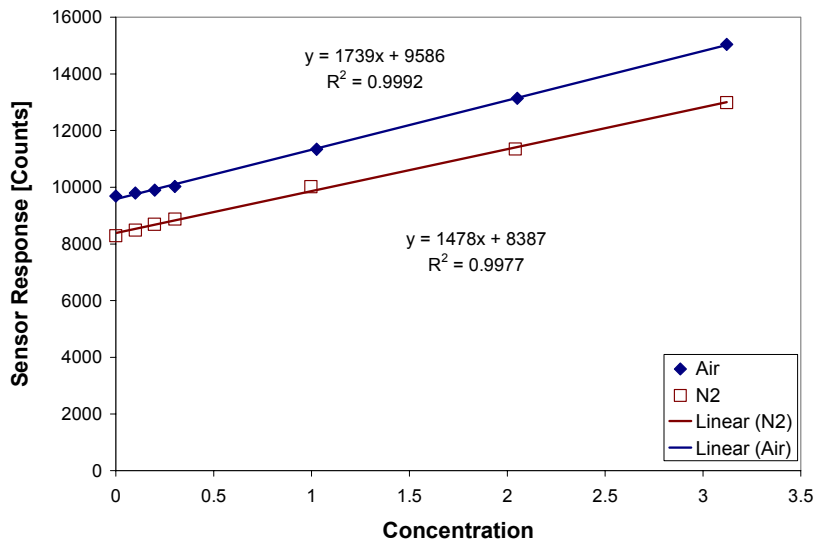


Figure 10. Sensitivity in N2 vs sensitivity in air.

In addition to ethylene there are other gases that tend to react on our catalyst potentially causing interference. The extent of interference is determined from the sensitivity of the sensor to these other gases at the operating conditions corresponding to ethylene. One gas that has been explored here is carbon monoxide due to concern about the presence of CO in the air generated by the fork lifts and agricultural equipment. A test was performed using the mixing apparatus and an additional cylinder containing 10 ppm carbon monoxide in nitrogen. The results of these tests are shown in Figure 11. The results show that although there is some sensitivity to carbon monoxide, the sensor is more than 40 times more sensitive to ethylene than to CO. This suggests that interference from carbon

monoxide is not a significant issue, unless the levels of carbon monoxide are extremely high (higher than the EPA set hazard threshold) or the ethylene measurement requirements are in the 10-ppb level.

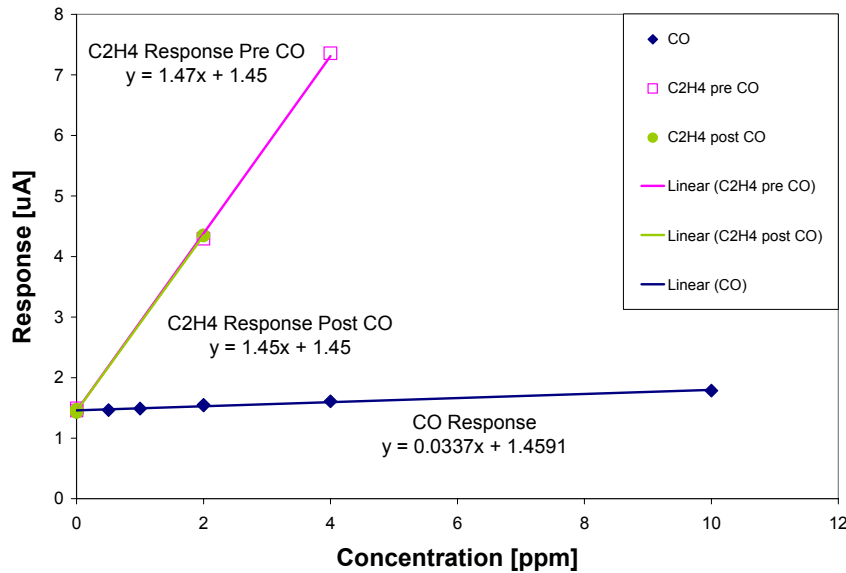


Figure 11. Sensitivity to carbon monoxide.

We also tested our sensor against a gas chromatography system, which is currently the “gold standard” in ethylene detection, for measuring the ethylene produced by a single apple (Figure 12). Single apples were placed in 0.5 liter jars and allowed to build up ethylene in the head space of the jar for several hours. Using appropriate fittings, the ethylene containing air within the jar was then recirculated through the ETH-1010 ethylene sensor. As evidenced in this figure, the total time required to get reading from a single apple is just a few minutes, which shows the built up ethylene within each jar for the different apples. Because of the high sensitivity of ETH-1010, the rate of ethylene production during each run was also measurable (Insert).

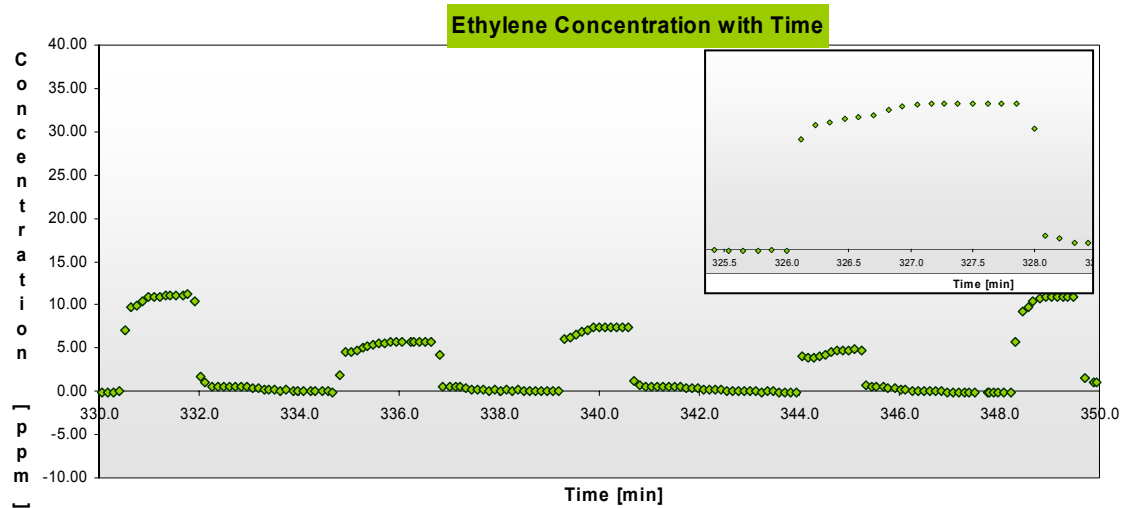


Figure 12. Time traces for single gala apple measurements performed at AgroFresh Wenatchee, October 2006 (Data provided with permission by Dr. Nate Reed).

Figure 13 shows an overlay of our sensor results and GC results for ethylene produced by a single apple. As you can clearly see, there is a correlation. One advantage to our sensor is that it can provide near real-time measurement of ethylene, which is much faster than the GC detection.

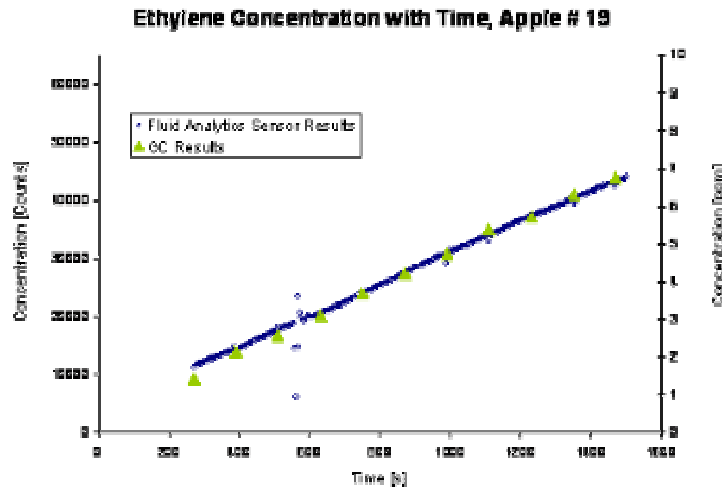


Figure 13. Single Apple Ethylene Generation Rate and Comparison with GC (experiments performed in collaboration with Dr. Dana Faubion at WSU Extension in Yakima, March 2006).

V. SUMMARY

In this report, we presented and discussed the results of our tests performed with a new electrochemical ethylene sensor prototype developed by Fluid Analytics, Inc. We showed that this sensor has the following attributes:

1. High sensitivity of down to 10-ppb;
2. Fast response of the sensor to the measurements (within seconds) and fast recovery (within a minute or so);
3. Low sensitivity to interferent gases such as carbon monoxide;
4. Higher sensitivity to ethylene in air than in an oxygen-deprived environment (pure nitrogen);
5. More than two times higher sensitivity to ethylene at room temperature than at cold storage temperatures;
6. Sufficient sensitivity and response rate to measure single apple ethylene production rates;
7. Portable and easy to use for laboratory or field measurement of single apple ethylene generation rate or flow through measurements of ethylene concentration in cold storage facilities.

VI. ACKNOWLEDGEMENTS

Fluid Analytics would like to thank the commission for providing this and other funding for advancing our sensor development and qualification testing both in the laboratory and in the field. The PI would also like to thank the technical contributions provided by Dr. Dana Faubion and Dr. Nate Reed.